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Purification of Heavily Contaminated Water -Practical Experience from the Treatment of Gaswork Site Groundwater and Anaerobic Digester Effluent

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1 Introduction

Anthropogenic impact causes water pollution beyond the ordinary biological cycle; therefore self-purification is often insufficient for treatment. While municipal sewage has a moderate load of common contaminations, industrial processes can be a source of numerous different pollutants in a wide range of concentrations. These diverse contaminations demand a variety of very different processes for adequate treatment. Biological, chemical and physical methods have been developed to remove these contaminants; often a combination of several methods is necessary to achieve the purification goals.

This thesis reports on research conducted to find and optimize treatment methods for two distinct types of heavily polluted water. The aim of this text is to provide background information and an overview of the findings. Further details can be found in the scientific publications, which are included.

The effluents treated herein are a) the groundwater from a former gaswork site, and b) the effluent of an anaerobic digester for biogas production. The contaminations of these effluents are very different. The carbon compounds of the contaminated groundwater are rarely found in nature, but they are very toxic; even carcinogenic and mutagenic. The contaminations of the digester effluent are very common, but in an unusual high concentration. Both contaminations are side products of the production of gaseous energy carriers, coal gas and biogas. These two sources of energy reflect the current change in energy policy - away from fossil fuels and towards renewable sources that lower the release of greenhouse gases. Even as policy makers promote energy efficiency and saving, the consumption of energy still increases. In addition, even while the employed techniques become more environmental friendly, there will always be undesired by-products.

Manufactured Gas Plants (MGP) were no exception. They not only produced town gas but also several by-products. Starting at the end of the 19th century, for more than six decades, manufactured gas was the prime energy source in urban areas for heating, lighting and cooking. Town gas was produced from coal by "dry distillation", the heating of coal. After the gas cooled down, several by-products condensed. These by-products, many of them highly carcinogenic carbon compounds, often made their way into the soil and groundwater underneath. Therefore, every MGP site is/was designed as a contaminated site and requires remediation.

Biogas is becoming increasingly important throughout the last 20 years, not only for supplying sustainable energy, but also for waste management. Biowaste, amongst other biodegradable sources, is fermented in anaerobic reactors, thereby producing biogas, which mainly consists of methane and carbon dioxide. This biogas is then combusted to generate heat and electricity. Hence, much of the organic load in these substrates is turned into biogas, while other compounds, as e.g. nutrients, remain highly concentrated in the anaerobic digester effluent. This effluent was traditionally used for manuring, but it has to obey legal limits for nutrients fertilization - imposed to protect the groundwater. Alternative ways for the management of this effluent are now investigated to make biogas production sustainable throughout the whole process.

The gaswork site groundwater and the anaerobic digester effluent both required an elaborate treatment to achieve removal of the contaminants. Several methods were combined and tested in laboratory and pilot scale. The results of these experiments led to nine scientific publications, which are assembled for this cumulative dissertation.

1.1 List of Publications

The list below presents nine publications that form part of this dissertation. The following summary recapitulates scopes, methods and results of the listed papers. References are given to look up details in the relevant paper.

Ι	Pilot plant experiences using physical and	Journal of Hazardous Materials,	1^{st}
	biological treatment steps for the remediation	163	Author
18-27	of groundwater from a former MGP site		
II	Ammonium Removal from Anaerobic	Water Science and Technology	1 st
28-39	Digester Effluent by Ion Exchange	(accepted)	Author
III	MGP Groundwater Treatment: Evaluation of	Gasworks Europe, Vol. 56,	1 st
	Physical and Biological Treatment Methods		Author
40-48	Including a Polishing Pond		
IV	Microfiltration and Ultrafiltration in the	IWA Membrane Conference,	1^{st}
49-55	Treatment of Anaerobic Digester Effluent	Moscow/RUS: Proceedings	Author
V	Pilot plant results for groundwater	Land Contamination &	2 nd
	remediation at the former gas work site	Reclamation, 14 (2)	Author
56-60	"Leopoldau" in Vienna, Austria		
VI	Comparing central and peripheral anaerobic	Water Science and Technology,	2^{nd}
	digestion of stillage from a large-scale	58	Author
61-67	bioethanol plant to animal feed production		
VII	Air stripping of ammonia from anaerobic	International Conference on	2^{nd}
	digestate	Nutrient Recovery From	Author
		Wastewater Streams,	
68-82		Vancouver/CAN: Proceedings	
VIII	Comparing Digestate Treatment Options for	16 European Biomass	2^{nd}
	the Anaerobic Digestion of Stillage at a Large	Conference, Valencia/ESP:	Author
83-86	Scale Bioethanol Plant	Proceedings	
IX	Post-treatment methods for groundwater from	Science of the Total	1 st
87-101	former manufactured gas plants (MGP)	Environment, Submitted	Author

2 Origin of Contaminations

2.1 Manufactured Gas Production

Manufactured gas, a flammable gaseous fuel, is originally a by-product of the coking process. Coal or oil were heated in a retort and the crude gas was passed through a condenser to remove tar and through a scrubber to remove other impurities. The residue remaining in the retort was coke. The development of manufactured gas paralleled that of the industrial revolution and urbanization in the 19th and early 20th century. Town gas is a more general term referring to manufactured gaseous fuels distributed by pipes in municipalities and used for lighting, cooking and heating. Other common terms are coal gas, syngas, hygas, and producer gas. Coal gas plants are commonly referred to, by environmental professionals and within the utility industry, as Manufactured Gas Plants or "MGPs." The by-products, coal tars, sulfur and ammonia, were a chemical feedstock for the dye and chemical industry, but also harmful contaminants in soil and groundwater of MGP sites. The discovery of large natural gas resources in the 1960s led to the replacement of manufactured gas. Depending on the processes, type of coal and the temperature of carbonization used for its creation, coal gas is a mixture of calorific gases with small amounts of non-calorific gases - carbon dioxide and nitrogen - as impurities.

Hydrogen	H ₂	50%
Methane	CH ₄	35%
Carbon monoxide	CO	10%
Ethylene	C_2H_4	5%

Typical composition of manufactured gas:

The first use of town gas in Vienna dates back to 1818. In the following years, many small manufactured gas plants supplied coal gas to single buildings or a few lamps. In 1842 the English Inter-Continental-Gas-Association (ICGA) bought those facilities and became the price-regulating monopolist. This situation became intolerable and in 1896 the municipality of Vienna decided to build their own MGP. In only three years, the MGP Simmering was finished and originally distributed 432,000 m³/d town gas. Due to increasing demand, the Simmering plant was constantly enlarged. In 1911, the MGP Leopoldau became the 2nd large gas work of Vienna. From 1969 until 1978, town gas was gradually substituted with natural gas and the gasometers served as gas storage vessels until their final shut down in 1985. In 1999, reuse concepts for business and housing started. The MGP site Simmering was assigned as a brownfield of the highest priority according to Austrian law ALSAG in 2000 [I, p3]. The remediation of these contaminated sites is a legal requirement demanding high standards compared to many other countries.

2.2 Biogas Production

Biogas generally refers to a renewable fuel emerging from anaerobic degradation, which is the biological breakdown of organic matter in the absence of oxygen. The less common wood gas which is created by gasification of wood or other biomass is not topic of this thesis, but biogas from anaerobic digestion. It is produced by fermentation of biodegradable materials such as biomass, manure or sewage, municipal waste, green waste and energy crops.

The composition of biogas varies regarding the origin of the anaerobic digestion process. Landfill gas typically has methane concentrations around 50%. The advanced waste treatment technologies relevant for these investigations can produce biogas with 55-75% CH₄, depending on the input material.

Methane	CH ₄	50-75 %
Carbon dioxide	CO ₂	25-50 %
Nitrogen	N ₂	0-10 %
Hydrogen	H ₂	0-1 %
Hydrogen sulfide	H_2S	0-3 %
Oxygen	O ₂	0-2 %

Typical composition of biogas:

The gases methane, hydrogen and carbon monoxide can be combusted. The energy release allows biogas to be used as a fuel for any heating purpose or it can be compressed and used to power motor vehicles. Austrian biogas plants mostly employ combined heat and power engines, to generate both heat and electricity.

2.3 General Relevance of Gaseous Energy Carriers

An energy carrier is a substance or phenomenon that can be used to produce mechanical work or heat or to operate chemical or physical processes. Gaseous energy carriers are frequently used, since they are easily transportable in pipes and convenient for storage, where their volume can be reduced by compression. The mechanical energy of wind and pressurized air can be utilized, e.g. to generate electricity, and therefore they also range amongst gaseous energy carriers. But combustible gases are of larger importance due to their high energy density. The most important gaseous energy carrier is natural gas; it has a higher energy density than petrol, but lower than hydrogen (13.9 kWh/kg, 12.7 kWh/kg, 33.3 kWh/kg, respectively). Natural gas is a fossil fuel, hence non-renewable, but unlike other primary energy carriers, it must not necessarily be converted into a secondary energy carrier (e.g. electricity). It can be directly used in households for heating and cooking, therefore gas distribution systems are operated in most urban areas all over the world. Recently, gas also becomes relevant as fuel for motor vehicles. Cars powered by natural gas, biogas or hydrogen still have market shares < 1 %.

Natural gas accounts roughly for 20 % of Austria's total energy demand. 15 - 20 % of this gas is used for the generation of electricity. Austrian biogas plants produce 83 million m³ biogas per year, while the consumption of natural gas is 10,000 million m³ per year. An important reason to reduce fossil fuels and increase the usage of renewable energy sources is climate change, affected by green house gases. Cow manure releases methane, which has a 22fold higher greenhouse effect than carbon dioxide. Therefore, the usage of co-digestion biogas and thereby oxidising methane is even more requested.

Following this trend, biogas has become an increasingly important source of alternative energy all over the world. In India and China thousands of small rural plants supply the heat and cooking energy for one household. In Austria, the number of biogas plants almost tripled within the last 5 years from 119 by the end of 2003 to 342 plants by mid 2008. Also the size of the plants increased, as their output shows: the electricity production augmented from 42 GWh in 2003 to 503 GWh in 2008, which is 0.9 % of the Austrian electricity demand. The majority of the Austrian plants are in rural areas, operated by farmers in cofermentation with manure and organic solids, such as plants (biomass) or biowaste. The biogas mostly fuels combined heat and power engines, the electricity is usually fed into the public grid, and the feed-in tariffs are legally regulated. Currently, biogas is not often fed into the gas distribution systems, since elaborate purification of the gas would be necessary.

3 Substrate treated: MGP Groundwater and Anaerobic Digester Effluent

3.1 MGP groundwater

Former gasworks or manufactured gas plant (MGP) sites are recognized as extensive sources of groundwater and soil pollution. The contaminations are various petroleum hydrocarbons, deriving from coal tars and other residues that were often stored and disposed of at such facilities. These pollutants typically include polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylene (BTEX), phenolic compounds, and inorganic compounds, such as heavy metals, cyanides, sulfides and ammonium. PAHs are a big group of chemical compounds that consist of fused aromatic rings. They are of special concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic. The larger the PAH molecules are, the less they are water soluble, which means, that their degradation takes very long time. BTEX are derivates based on one aromatic ring only, but also have harmful effects on the central nervous system. Due to their high volatility they easily evaporate from groundwater into air. Because of their toxic effects, the legal limits for all these substances are very low. Phenol is also suspected carcinogenic, while other substances, such as tar and sulfur are less harmful. But the latter can cause operational problems by forming polymers and thereby clogging pipes and valves. The concentrations of typical MGP compounds as well as sum parameters, e.g. HC-Index, total organic carbon (TOC) or chemical oxygen demand (COD) were analyzed and compared with legal limits [I, p23]. The groundwater was pumped up by extraction wells and treated on site (pump-and-treat system). This purification process is less costly than ex-situ remediation techniques [1, p21]. Pump-and-treat cannot achieve full remediation, but is a useful additional method for hydraulic control by interrupting the groundwater flow and thereby prohibit contaminant migration.

Parameter	PAH [µg/l]	Naphtaler [µg/l]	ne Benzo(a [µg	Benzo(a) pyren [µg/l]		enzene [µg/l]	BTEX [µg/l]		Phenols [mg/l]	(Cyanide [mg/l]		
Well 1	789 - 865 ^a	608	<0,	<0,03		<0,03		56 - 512	742 - 806	0,	$04 - 0,08^{b}$	0,1	$8-0,25^{\circ}$
Well 2	216 - 745 ^a	66	<0,	03	247 - 547		271 - 635	0,	21 - 0,53 ^b	0,0	$0 - 0,18^{\circ}$		
Parameter	TOC [mg/l]	COD [mg/l]	HC [mg/l]	NH4 ⁺ [mg/l	-]	NO ₂ ⁻ [mg/l]	Fe ²⁺ [mg/l]		Mn ²⁺ [mg/l]		S ²⁻ [mg/l]		
Well 1	6,0-6,4	24 - 37	2,4-3,0	3,1-3	,9	<0,01	2,7-3,2	2	0,35 – 0,46	3	3,12 - 3,48		
Well 2	4.32 - 13.0	21 - 61	0.21 - 1.1	3.2 - 7	.1	< 0.01	0.24 - 0.4	18	0.12 - 0.21		9.9 - 17.6		

Groundwater quality in well 1 and well 2 at the MGP site Simmering, supplying the groundwater for the experiments

^a sum of EPA 16

^b phenol analytics provided by Geoscience Center Goettingen, Germany

^c easily purgeable cyanides

3.2 Anaerobic Digester Effluent

While the number of biogas plants roughly tripled within 5 years, the electricity output increased to more than a 10fold. This means, not only the number, but also the size of the plants increased. Often fed with supraregional substrates, not only more biogas, but also massive amounts of digester effluent are produced, being still rich in organics and also in nutrients. The concentrations of nitrogen, mainly present in the form of ammonia, can be more than 100fold higher than in municipal waste water. Nutrients in water bodies promote algal growth (eutrophication), which is then followed by oxygen consuming degradation, thereby killing aquatic life. Also ammonium has a high oxygen demand for biological removal. Ammonia toxicity to fish and other aquatic animals is very significant and concentrations in the range 0.2-0.5 mg/l can be fatal.

The disposal of these residues has become the bottle neck of this sustainable energy source. Traditionally the digestate was used for manuring. However, due to the legal limits for N-fertilization per area of farmland (DüngemittelVO, 1994 – Austrian Law for Fertilizer Output), imposed to protect the groundwater, increasingly big areas are required and rising transport costs would emerge. An alternative option is to separate the solid residues from the liquid fraction that contains the major amount of the nitrogen. The less voluminous solids are whether directly used for fertilizing or composted, since aerobic treatment can further degrade substances which are anaerobically not degradable anymore. A further option is to dry and burn the biosolids. The liquid fraction contains the main part of nitrogen and many other nutrients; therefore it has to undergo further treatment. In current research, several methods are tested to purify this particular challenging liquid.

Effluents for this thesis were obtained from a 500 kW (electricity) biogas plant in Styria/Austria. It is operated in co-digestion mode with cow manure (50 %), kitchen and bio waste (25 %), slaughter waste (15%), and energy crops (10 %) as a substrate. The effluent is rich in nutrients, particularly nitrogen, but also phosphorus and potassium. These are the key elements of fertilizers, and therefore manuring was the traditional usage of digestate. The 500 kW plant roughly produces 50 t nitrogen per year and therefore would require a land area of 300 hectare (3 km²) for fertilizer application. Hence, the removal of ammonium from digester effluent was of particular concern in this thesis. Other relevant elements in the effluent are potassium, phosphorus, calcium, magnesium, sulfur and sodium [II, p31].

	TS [%]	TN [mg/l]	NH ₄ -N [mg/l]	COD [mg/l]	P [mg/l]	K [mg/l]
Digester Effluent	5.05	9,326	7,194	54,460	1382.00	2,344
After Solid Sep.	4.95	8,818	6,640	47,870	1365.46	2,971
After Micro Filt.	1.04	5,406	5,279	2,264	3.23	2,205
After Reverse Osm.	0.00	482	467	95	1.07	85
After Ion Exchange	0.00	482	467	95	1.07	85

Parameters of the Anaerobic Digester Effluent throughout the treatment process (total solids, total nitrogen, ammonium nitrogen, chemical oxygen demand, phosphorus and potassium)

4 Adequate Treatment

The relevant wastewater streams, MGP groundwater and anaerobic digester effluent, were very challenging to purify. Since both wastewater streams have very different contaminations, also differing problems had to be overcome, which required various treatment methods. The carbon compounds of the contaminated groundwater are rarely found in nature, but are very toxic, even carcinogenic. Therefore the remediation goals are very strict and very sensitive techniques were necessary to achieve these goals.

The contaminations of the digester effluent are very common, but in an unusual high concentration, which then is again corrosive and toxic. Sturdy methods were tested to remove these bulk contaminations in the most economic way. From a wide range of purification techniques, the best solutions regarding technical feasibility and costs had to be chosen. Since MGP remediation is very site-specific and anaerobic digester effluent treatment is a fairly new topic, not much relevant experience was available. After a pre-selection based on literature research, the evaluation of the methods had to be based on experimental results. This procedure follows the "trial and error" approach, which is the usual case for unknown substrates/topics. Not a single treatment technique, but several different methods were necessary to achieve the remediation goals. To control this sequence of process steps, programmable logic controller (PLC) were employed at the pilot plants, data about certain parameters were recorded automatically every hour [I, p24]. The pilot plant stage is an important part for implementing such technologies, since each of these plants is a unique case [I, p21]. No general rule applies, since the conditions and circumstances may differ widely.

A few facts to consider for MGP site remediation:

- What contaminants occur
- What are their concentrations
- Soil characteristics (organic/inorganic)
- Groundwater flow: direction, velocity
- Aquifer characteristics
- Surroundings infrastructure, site usage
- Third party issues
- Disposal of soil, contaminants
- Legal requirements

Also for anaerobic digester effluent purification, numerous facts are to consider, especially, since it is a new topic of research, and not much previous experience is available. In future, more standardized processes can be expected, but the treatment will remain site-specific. The following issues are of importance:

- Concentration of organics, nutrients
- Amount of digester effluent
- What substrate is used
- Where is the substrate from
- Area available for manuring
- Other usage for manure
- Transport costs, distances

Lab scale investigations cannot take all these circumstances into consideration. Therefore a pilot plant stage is necessary for their evaluation. Furthermore the testing of the technical feasibility is a crucial point. During the pilot stage, many breakdowns and problems occurred, which were then overcome with appropriate solutions. These experiences help avoiding such problems in full scale, where the fixing would be much more costly. The outcome of these experiments is a recommendation for two specific practical applications, since this is applied research.

5 Investigated Purification Methods

The contaminations of the wastewaters treated herein are either unusual or in very high concentrations. Hence, adequate means have to be applied to achieve sufficient purification. A diversity of pollutants is present in a single liquid; therefore the purification often requires several different methods which are applied in sequence. In order to operate a purification plant under stable conditions, it is necessary to remove as much pollution as possible with sturdy, cheap techniques, before more sensitive or expensive means have to be applied to fulfill the remediation goals [I, p30]. Effective pre-treatment is critical for both successful purifications can clog pipes and valves at the MGP remediation, whereas solids can significantly reduce the efficiency of membranes at the purification of digester residuals. The following list compiles the treatment methods which proved to be appropriate for the two particular applications, based on experimental results. The techniques are divided into physical, chemical and biological removal processes.

5.1 Physical Treatment

5.1.1 Sedimentation/Flotation

A sedimentation separates particles of higher density from suspensions. Due to gravity, these particles sink down, a low flow velocity is necessary to allow settling. Flotation uses the contrary effect, lighter particles float on the surface, where they can be removed by a skimmer. Aeration enhances the sedimentation/flotation process [Description: I, p20].

Appropriate pre-treatment turned out to be a critical issue to achieve good results in MGP groundwater purification and to ensure stable operation conditions. A robust sedimentation/flotation fulfilled this purpose. It could be easily maintained and allowed simple removal of float or settleable precipitates. A HRT > 3 h is recommended to provide sufficient time for completion of precipitation reactions of sulfur or tar polymers in order to protect the following reactors from clogging [I, p26; III, p48; V, p59].

5.1.2 Screw Press

A horizontally arranged conical screw continually feeds anaerobic digester residues through a perforated cylinder made of stainless steel. Increasing pressure squeezes the water through the perforation holes; additionally flocculants can be applied for improved particle removal [Description: II, p29].

The screw press (mesh size = 1 mm) used herein removed solids from anaerobic digester effluent at low energy consumption. It proved to be a simple, reliable and sturdy device. The separated solids had a TS around 21 % and were convenient for any further manipulation [II, p29; IV, p50].

5.1.3 Vibration Screen

A horizontal sieve is given an oscillating motion from vibrators, thereby separating the oversize from the throughput. Vibration screens have low energy consumption, are simple in handling, periodical cleaning of the screen is necessary [Description: II, p29].

A vibration screen (mesh size = 0.25 mm) was used in these experiments as an additional device to improve the solid separation from anaerobic digester residuals after the screw press. It turned out to be reliable in operation [II, p29; IV, p50].

5.1.4 Multi-Media Filter (MMF)

A multi-media filter consists of layers of sand or anthracite with different corn size. These layers build a filter to remove particles from a suspension. The flow regime is mostly top-down. Once, these particles limit the flow and build up pressure, a backflush is necessary to regenerate the filter [Description: I, p20].

In MGP groundwater remediation, the multi-media filter was necessary to remove particles before they get into the granulated activated carbon filter. Even the operation was without major problems, the MMF exhibited a certain deficit to protect the GAC of flocs which are eluted of the previous biological stage. The reason is presumable the fine dispersed character of the sulfur precipitates. [I, p22,26; III, p43]

5.1.5 Membranes (MF, UF, RO)

A membrane is a layer of material which serves as a selective barrier between two phases and remains impermeable to specific particles, which are retained and accumulate in the retentate (concentrate) stream. The permeate (filtrate) stream contains the components which are allowed passage by the membrane. Artificial membranes can be produced from organic materials such as polymers as well as inorganic materials. Most of the commercially utilized synthetic membranes in separation industry are made of polymeric structures. Ceramic membranes are more resistant than polymeric membranes. They are produced from inorganic materials such as aluminium oxides, silicon carbide, and zirconium oxide. The most commonly used driving forces of a membrane process in industry are pressure and concentration gradients. Reverse osmosis processes are operated under high pressure up to 100 bar, therefore require much pump energy. Backwashing and less frequently chemical cleaning are necessary to ensure the flux $[1/m^2/h]$ through the membrane. According to their size exclusion, the membranes are divided into microfiltration (MF; pore size = $0.1 - 1.0 \mu m$; cutoff = 500,000 Dalton), ultra filtration (UF; 0.01 - 0.1 µm; 100.000 Da) and reverse osmosis (RO; 0.001 µm; 100 Da). MF completely removes suspended solids, UF achieves colloid removal and RO can even separate salts. 10 - 20 % of the inflow of a membrane processes remains as concentrate/retentate, often highly concentrated with salt. The usage or disposal of this concentrate has to be considered beforehand [Description: IV, p50].

In these experiments, different organic and inorganic membrane materials with different pore sizes were compared, a complete list can be found in IV, p51. Tests under various conditions revealed, that crossflow tube membranes provide a more stable operation than the submerged hollow fiber module. The membrane with a pore size of 20 kDa proved to be more efficient than larger pore sizes of 80 kDa, 100 kDa and 250 kDa, since the particles are too big to clog these pores. A flux of 18.3 l/m²/h at 2.0 bar transmembrane pressure was achieved, the crossflow velocity was kept at 4 m/s. The contaminant removal showed satisfactory results in COD and TP removal, while ammonium could not be reduced much. Despite higher pump energy consumption and smaller membrane area, UF tube modules are recommended, since they provide a stable process and a good effluent quality [IV, p50-53].

5.1.6 Ion Exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'. Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. The process itself is simple and reliable, the effluent quality very satisfactory. For exchanger regeneration, chemicals are used, forming a concentrate with the removed ions [Description: II, p30].

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. For the ion exchange experiments herein, clinoptilolite and polymeric resins were compared. Clinoptilolite belongs to zeolites, a group of naturally occurring alumino silicate, and it has the highest ammonium exchange capacity amongst this group. Polymeric ion exchange resins have even higher cation exchange capacities, higher reaction rates and chemical resistivity. A list of the applied ion exchange materials can be found in II, p31. Ion exchange requires a good pre-treatment and can only be employed for final removal of eg ammonium cations. As a final treatment step, ion exchange proved to be a successful and stable process with very satisfactory effluent quality. The legal limits for disposal into public water bodies could be met by both the polymeric strongly acidic resins and clinoptilolite, while the nutrients were recovered in the washing brine. Due to higher exchange capacities, reactivities and sufficient durabilities, the polymeric resins are more recommendable than clinoptilolite. Ammonium removals of more than 99 % were achieved. The regeneration with acid containing a 3fold stoichiometric ratio of protons is sufficient to maintain the cation exchange capacity. This washing brine has to be disposed or used, eg it can be mixed with cow manure to improve the nutrient value [II, 32-38].

5.1.7 UV Irradiation

UV irradiation can be an effective viricide and bactericide. It is frequently used in wastewater treatment in countries as e.g. the USA, but not in Austria, where it is commonly applied in drinking water treatment. Also many bottlers of spring water use UV disinfection equipment to sterilize their water [Description: IX, p91].

UV irradiation was applied to decrease the bacterial count in the biologically treated MGP groundwater. It demonstrated high efficiency, but the initial effect was not sustainable, and bacterial growth quickly re-initiated. This effect would likely stimulate biological clogging of infiltration wells when effluent is re-injected, and therefore UV irradiation is not recommended [III, p46,47; IX, p98,99].

5.1.8 Stripping

Stripping is a physical separation process where one or more components are removed from a liquid stream by a vapor or gas stream. In industrial applications the liquid and gas streams can have concurrent or countercurrent flows. In these experiments, hot air was used in concurrent flow mode. Stripping is usually carried out in either a packed or trayed column. Stripping works on the basis of mass transfer. The idea is to make the conditions favorable for the component, A, in the liquid phase to transfer to the vapor phase. High temperature and high pH play the key role, as they influence the dissociation equilibrium of NH_4^+/NH_3 and thereby shift the distribution of ammonia towards the gaseous phase. [Description: VII, p70]

The alkalinity of the digester effluent, i.e. the HCO_3^- concentration, was identified to be of critical importance for efficient ammonia stripping. On the one hand it acts as a buffer system which makes elevation of the pH more difficult on the other hand the parallel desorption of CO_2 during NH₃ stripping stabilizes the pH. It was demonstrated that precipitation with lime milk (Ca(OH)₂) for removal of suspended solids and carbonates results in a strong decrease of alkalinity. Hence the pH in the course of the stripping process drops strongly which leads to a lower process efficiency. Therefore lime milk has to be overdosed which leads to an excessive chemical demand. As alternative suspended solids removal by means of microfiltration is proposed. In this case, only a moderate pH adjustment with caustic soda to pH 10 is suggested. To compensate, a high temperature, 80°C, should be applied during to the stripping process. Under such conditions elimination rates of 90% and even higher were achieved [VII, p74-81].

5.1.9 Granulated Activated Carbon Filter (GAC)

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. Due to its high degree of microporosity, one gram of activated carbon has a surface area of approximately 500 m², as determined typically by nitrogen gas adsorption. Granular activated carbon has a relatively larger particle size compared to

powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system [Description I, p21].

In a MGP groundwater purification process, a granulated activated carbon is generally the last process step. On one hand the GACs absorb substances which have not undergone removal up to this point; on the other hand they provide a final safeguard in case previous treatment steps would fail. The experiments fulfilled these expectations, the GAC fully assured the effluent quality and the residual concentrations of the target contaminants were close to detection level. At the end of the experiments from both GAC filters several samples of the activated carbon at different filling levels were taken and the residual iodine adsorption capacity was determined to evaluate the maximum treatment capacity [I, p24; III, p43,48].

5.2 Chemical Treatment

5.2.1 Coagulation/Flocculation

Coagulation/Flocculation is a process where a solute comes out of solution in the form of flocs or flakes. Unlike precipitation, this reaction happens at a concentration generally below the solubility limit in the liquid. According to the IUPAC definition, flocculation is "a process of contact and adhesion whereby the particles of a dispersion form larger-size clusters." In colloid chemistry, flocculation refers to the process by which fine particulates are caused to clump together into a floc. This process improves the sedimentation or filterability of small particles. Particles finer than 0.1 µm in water remain continuously in motion due to electrostatic charge (often negative) which causes them to repel each other. Once their electrostatic charge is neutralized by the use of coagulant chemicals, the finer particles start to collide and agglomerate (combine together) under the influence of Van der Waals's forces. These larger and heavier particles are called flocs. Flocculants, or flocculating agents, are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Many flocculants are multivalent cations such as aluminium, iron, calcium or magnesium. These positively charged molecules interact with negatively charged particles and molecules to reduce the barriers to aggregation. In addition, many of these chemicals, under appropriate pH and other conditions such as temperature and salinity, react with water to form insoluble hydroxides which, upon precipitating, link together to form long chains or meshes, physically trapping small particles into the larger floc [Description: V, p58].

MGP groundwater purification by coagulation/flocculation with ferric chloride and flocculant aid was primarily performed on a laboratory scale. Good flocculation and contaminant removal was observed. At a concentration of 0.1 Mol/m³ Fe³⁺ as a coagulant with the support of 0.1 g/m³ flocculant aid, removal rates of 60 - 70 % were obtained for turbidity and mineral oils. As well 45 % of the PAHs were removed. However, it was not possible to repeat these promising results in pilot plant scale, due to the suboptimal system design and also due to fluctuation in influent composition [V, p59].

5.3 Biological Treatment

Aerobic wastewater treatment uses dissolved oxygen to promote the metabolism and growth of microorganisms to remove organic material. The microorganisms can be whether fixed on a surface or suspended in the liquid as in the activated sludge process, the most common process in wastewater treatment. Other common techniques are surface-aerated basins, filter beds, biological aerated filters, membrane bioreactors and rotating biological contactors. The experiments for MGP groundwater treatment employed a submerged fix film reactor (SFFR), a biological activated carbon filter and a polishing pond for the treatment of MGP groundwater.

The biological nitrogen removal (BNR) also requires oxygen, it consists of two steps: the aerobic nitrification converts ammonium into nitrate, and the anoxic denitrification turns nitrate into elementary nitrogen gas, which is then released into the atmosphere. BNR is commonly applied in municipal wastewater treatment. The high ammonium concentrations in anaerobic digester effluent may be inhibitory for microorganisms, hence biological treatment cannot be applied directly [II, p29]. Dilution would be necessary, which would not change anything about the high aeration costs. An additional carbon source to adjust the C/N ratio for the microorganism need would cause further costs. Direct disposal limits into water bodies are very hard to achieve with biological removal only. Therefore, the research of this dissertation focused on physical nitrogen removal methods as economically and environmentally friendly treatment alternatives.

5.3.1 Submerged Fixed Film Reactors (SFFRs)

Fixed Film reactors are filled with a filter media. The purpose of the package material is to support highly active biomass; the particle filtration effect is negligible. The media is either in suspension or supported by a porous layer at the bottom of the filter. Carbon reduction and ammonia conversion occurs in aerobic mode in a single reactor while nitrate conversion occurs in anoxic mode. The operation mode can either be in upflow or downflow configuration. While activated sludge processes work well for ordinary waste water, fixed biofilm reactors are less sensitive to variations in influent supplies and are also better adapted to groundwater with comparable low concentration of contaminants [Description: I, p20].

The chosen system turned out to be highly reliable and the SFFRs contributed much to the degradation of the typical MGP contaminants, such as PAHs, BETX, and aliphatic hydrocarbons. Expanded clay pellets as a packaging material was highly adequate, as confirmed by stable degradation rates throughout the whole operation period. The contaminants are retarded in the biofilm and therefore given more time for biological carbon reduction. The addition of phosphate showed no clear evidence of improved biological removal of contaminants, even while the COD:N:P ratio might suggest so. According to these pilot plant experiments, it is suggested for the full scale plant to establish a counter-current flow regime instead of the applied co-current flow. This would leave tar precipitations at the top layer where they can be easily removed. Furthermore the aeration devices at the bottom would not be affected by deposits as observed in the pilot plant [I, p22,26; III, p43,48].

5.3.2 Biological Activated Carbon Filter

The activated carbon in the filter not only absorbs hydrophobic contaminants, but also provides the surface area for biofilm growth. The microorganism degrade contaminations by aerobic metabolism, therefore an aeration device is required. Ideally, the chemical/physical and the biological pollutant removal support each other. The activated carbon absorbs shockloads and retards contaminants to give more time for biological degradation, and the latter again regenerates the capacity of the activated carbon, or at least prolongs the lifetime of the filter [Description: V, p58].

The pre-requisite for successful MGP groundwater treatment with a biological activated carbon filter was a proper nutrient supply and sufficient oxygen availability. With the subsequent activated carbon filter (not biologically activated), it was possible to achieve drinking water level, with regard to the Austrian regulation, for the target components PAHs, BTEX and mineral oil. In the investigated case these components were relatively easily biodegradable and rapid biological breakdown occurred. By this effect, termed bioregeneration, the lifetime of a GAC filter can be extended and the activated carbon require less frequent regeneration [V, p59,60].

5.3.3 Polishing Pond

Biological degradation has the potential to fully remove contaminations. This is important for MGP contaminats, since many of them are carcinogenic, mutagenic or teratogenic. A polishing pond was installed as final biological process step of the pump-and-treat system. By doing that, further pollutant removal should be achieved at low costs, since the operation of a polishing pond is a reliable and inexpensive process step. Oxygen is provided by algal photosynthesis. Introducing serveral plants from an adjacent wetland also served as inoculation for numerous aquatic and sludge-inhabiting animals. A rich biodiversity established within short time [Description: IX, p89].

Chemical analysis revealed, that the polishing pond did not contribute much to the pollutant removal, but two of the four ecotoxicity tests appeared to indicate that the polishing pond may have provided some improvement to the overall ecological health of the effluent. Even though only minor contaminants removal was achieved in the polishing pond, it proved to be useful as an instrument for "biological monitoring": an impressive diversity of aquatic life developed within short time and made the achievement of a good groundwater remediation visible for regulators and non-experts alike [III, p44,48; IX, 92-100].

6 Remediation Goals Achieved

6.1 Legal Remediation Goals

Remediation goals are defined by the law in accordance with the final usage/disposal of the effluent. For discharge of the treated MGP groundwater three different options were considered with increasingly stringent legal standards: disposal into i) sewer, ii) public water, or iii) recharge into groundwater. The pump-and-treat system used herein performed well. By employing an aerated sedimentation, a submerged fixed film reactor (SFFR), a multi-media filter and an activated carbon filter, the water quality for disposal into open water bodies could be achieved [I, p 27].

Discharge for anaerobic digester effluent also has to meet legal limits, whether it is applied on farmland or discharged into water bodies. If possible, the liquid should be used in internal recycling options as e.g. adjusting the total solids concentration in the anaerobic digester; irrigation of compost, biofilters; process water for backflushing, cleaning, etc. These options are always site-specific, no legal regulations are relevant, but still quality limits have to be met, e.g. to prohibit an increase of the salt concentration in the reactor. The treatment process at the biogas plant investigated herein consisted of a solid separation by screw press and vibration sieve, a micro filtration and a reverse osmosis. The effluent quality, set by the supplier of the prototype plant, could not be achieved, especially not regarding nitrogen [II, p29]. Further lab experiments with ion exchange greatly improved the quality and met the legal limits for discharge into public water bodies [II, p31].

6.2 Social Remediation Goals

Beside legal limits, social and ecological remediation goals become increasingly important. From a social point of view, the public acceptance of every process is crucial. If neighbors and third parties interests are not considered, expensive law suites may stop a process, which is technically already challenging enough. Proactive behavior, information and participation of involved parties are recommended to reduce these risks. In the case of the MGP site remediation, the polishing pond did not significantly improve the effluent quality, but it proved to be useful as an instrument for "biological monitoring": an impressive diversity of aquatic life developed within short time and made the achievement of a good groundwater remediation visible for regulators and non-experts alike. This result can be important to meet third party issues at remediation projects. Former MGP sites are located mostly in central and densely populated areas, and the ultimate remedy selection is often dependent upon public acceptance [III, p44,48; IX, p92-100].

In contrary, most biogas plants are operated by farmers in rural areas. Mostly only few neighbors are affected, often living in larger distances. Still certain social issues have to be handled carefully. Polluted, foamy influents into rivers and creeks are not acceptable and particularly odor emissions from plants immediately raise public awareness. Well operated bioreactors do not emit much odor, but still a good exhaust air management with appropriate filters is necessary beside effluent treatment. For MGP remediation, exhaust air is not only a nuisance, but the evaporating substances can be very harmful. Therefore sufficient air treatment is important.

6.3 Ecological Remediation Goals

While ecological awareness increases, also ecological remediation goals receive greater attention. Chemical analysis, mandatory by law, may not necessarily on their own be representative of the environmental risk. Therefore, ecotoxicity tests and aquatic biological community data may provide valuable and complementary information that can then be used to assess overall ecological risks posed by effluent streams. A good example was again the polishing pond at the MGP site. The big diversity of plants and animals in the pond made visible the achievements of good groundwater remediation. Although the abundance of certain species give information about the water quality, still these data are difficult to compare. Hence, several additional standardized ecotoxicity tests were applied. These complementary results proved the remediation success from an ecological point of view.

7 Conclusions

The chosen combination of purification techniques was successful for MGP groundwater treatment. The discharge requirements into public water bodies were achieved and the hydraulic containment was accomplished. Besides fulfilling legal limits, the obvious ecological remediation was very satisfactory. It is assumed, that such criteria will become increasingly important in the future. Although the pump-and-treat plant worked well, further measurements, focusing on soil treatment, are necessary for complete remediation of the site. The problem of anaerobic digestate management emerged during the last years. Since that time, progress has been made, and the experiments herein contribute to further advancing a this process. Still, further improvement, and therefore further research is recommended. Moreover, a critical evaluation of the whole biogas process is necessary, including all steps, as e.g. fertilizing, transportation and effluent purification. The consumption of (non-renewable) fuel and chemicals within these steps has to be implemented in an overall-efficiency balance. The social perspective is of equal importance as the economic: energy crop farming must not have a negative impact on food prices. Nutrition, especially basic food supply for low-income people, must always have higher priority than bioenergy production.

The abandonment of town gas generation and the increase of biogas production a few decades later reflect the current ecological trend – away from fossil fuels towards renewable energy sources. The reasons for this changed energy policies are mainly the increasing scarcity of fossil fuels, climate change and especially a movement towards sustainability. Town gas did not fulfill the latter criteria; it was used for 100 - 150 years, and the remediation of the MGP sites will probably take the same time. Nowadays, technologies are only appropriate if they don't have negative consequences for the future. Evaluations have to ensure beforehand that resources are not exploited and contaminations will not be left to following generations. Biogas is part of the natural carbon circle and therefore is a renewable energy source. However, it should be emphasized that adequate treatment or recycling of all sidestreams and by-products needs to be implemented in order to create a "zero emission plant" and to make this way of energy production sustainable.

Pilot plant experiences using physical and biological treatment steps for the remediation of groundwater from a former MGP site

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ABSTRACT

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Keywords: Groundwater remediation MGP Contamination Pilot-scale Pump-and-treat The production of manufactured gas at a site in Vienna, Austria led to the contamination of soil and groundwater with various pollutants including PAHs, hydrocarbons, phenols, BTEX, and cyanide. The site needs to be remediated to alleviate potential impacts to the environment. The chosen remediation concept includes the excavation of the core contaminated site and the setup of a hydraulic barrier to protect the surrounding aquifer. The extracted groundwater will be treated on-site. To design the foreseen pumpand-treat system, a pilot-scale plant was built and operated for 6 months. The scope of the present study was to test the effectiveness of different process steps, which included an aerated sedimentation basin, a submerged fixed film reactor (SFFR), a multi-media filter, and an activated carbon filter. The hydraulic retention time (HRT) was 7.0 h during normal flow conditions and 3.5 h during high flow conditions. The groundwater. However, it was also demonstrated that appropriate pre-treatment was essential to overcome problems with clogging due to precipitation of tar and sulfur compounds. The reduction of the typical contaminants, PAHs and BTEX, was more than 99.8%. All water quality parameters after treatment were below the Austrian legal requirements for discharge into public water bodies.

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1. Introduction

1.1. Soil and groundwater contamination from gasworks sites

Groundwater contamination by various anthropogenic organic compounds is a widespread problem in industrialized environments [1–5]. Especially former gasworks or manufactured gas plant (MGP) sites are recognized as extensive sources of soil and groundwater pollution [6,7]. Former MGP sites are contaminated with various hydrocarbons derived from by-products such as tars and other residues that were often stored and/or disposed of at such facilities. Typically contaminants include polycyclic aromatic hydrocarbons (PAHs), BTEX, phenols and various inorganic contaminants [8–12].

1.2. Approaches for remediation of MGP sites

Remediation of former MGP sites typically comprises activities for source removal or control and for the cleanup of contaminated groundwater. With regard to cleanup efficiency, it is clearly advisable to remove the core contamination from the subsurface if that is possible. However accurately localizing non-aqueous phase liquids (NAPLs) in the subsurface may be very difficult [13]. Excavation and subsequent ex situ treatment are very expensive techniques. The extracted soil has to be washed, treated thermally, or else safely disposed. The costs for hazardous waste landfills have been increasing. Therefore more economical methods are favored such as pump-and-treat, in situ thermal desorption, biological treatment, and water-based soil washing [13]. Other techniques aimed at volatilization of organic contaminants from soils (e.g. steam stripping or vapor extraction) are not expected to be effective for removal of the high molecular weight, low volatility tars encountered at MGP sites [13]. Generally, ex situ techniques are more costly and cause a severe disruption of the environment. Sometimes ex situ techniques cannot be applied if access to the contaminated soils is limited due to existing structures.

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Groundwater pollution causes further migration of contaminants and is of concern due to the potential impact of contaminating drinking water supplies over a large area [14]. Plumes of contaminants can extend 0.5-10 km from their source, even though the migration of the contaminants is slower than the groundwater velocity. Theses plumes form over decades and are common in North America and Europe, A series of recovery (extraction) wells or interceptor trenches can be implemented for continuous pumping of contaminated groundwater. In addition, monitoring wells and injection wells for infiltration may be necessary. This provides hydraulic control of subsurface contaminants to prevent their migration [15]. The contamination concentration of the extracted water often decreases initially, followed by a leveling of concentration and sometimes a gradual decline, which is generally expected to continue over decades [13]. This is due to the slow desorption and dissolution of certain contaminants (especially heavy components in NAPLs) in groundwater. Another limitation is, that the groundwater flows mainly in the high-permeability zones, while the low-permeability layers and lenses are flushed less effectively [16]. These mass transfer limiting processes result in long pumping times [17]. Projected time frames for pump-and-treat operations range from 10 years [18] to longer than 100 years [13]. In the case of former MGPs, remediation involving pump-and-treat has to be considered more as a hydraulic control than a complete remediation process [13,16,17,19-21]. Therefore pump-and-treat is conveniently combined with other remediation techniques.

1.3. Pump-and-treat concepts

The traditional pump-and-treat system comprises a series of recovery (extraction) wells or interceptor trenches to pump the contaminated groundwater from the subsurface for further remediation in a treatment plant. The mixture of various contaminants in the groundwater at former MGP sites requires several process steps. Typically, treatment involves a combination of physical, chemical, and biological methods, while the particular plant configuration is often site specific [13].

In a study at Griftpark, a gas work site in Netherlands, four different combinations of treatments were investigated. The preselection of treatment methods in the plant was based on a theoretical feasibility study in which all available methods were considered and several additional laboratory tests [22]. For initial treatment, stripping technologies were compared to fixed biofilm and activated sludge remediation. This first step was followed by coagulation, flocculation, or sedimentation. All combinations had a sand filtration and an activated carbon filter at the end of the treatment train. Sand filtration is an inevitable step for solids removal, before the activated carbon filter can be applied for final polishing [23].

As a result of the study of different process combinations, biological treatment is recommended as a core element of the treatment concept. Hydrocarbons (HC), especially smaller ones, have proven to be readily biodegradable under aerobic conditions [16]. While activated sludge processes work well for ordinary waste water, fixed biofilm reactors are less sensitive to variations in influent supplies and are also better adapted to groundwater with comparable low concentration of contaminants. The outer layers of the biofilm protect the inner cells from toxicity and reduce soluble contaminant concentration by adsorption [24]. Biofilms provide a high density of microorganisms, also the hydraulic retention time (HRT) can be low while maintaining high cell residence times. Within the different systems using fixed biofilms, submerged upflow fixed-film reactors (SFFRs) have proven to be most successful [12]. Rotating biological contactors with partially immersed disks or tricking filters are less efficient, while the disadvantages of fluidized-bed reactors are mainly the higher investments costs and the lack of stability [25,26].

In the investigated case, a combination of physical pretreatment, followed by biological treatment and finally absorption was chosen. A SHFR was employed using expanded clay pellets, commonly known under their brand name Leca, as a biofilm support material. A multi-media filter and granulated activated carbon filters (GACFs) were established at the end of the treatment process. On one hand the GACF absorb substances, which have not undergone removal up to this point; on the other hand they provide a final safeguard in case previous treatment steps would fail.

1.4. Aims and scope

In Austria, the remediation of contaminated sites is a legal requirement demanding high standards compared to many other countries [27]. The investigated former MGP site in Vienna, Austria with a size of 325,000 m² is situated in a groundwater stream, which is 300 m distance from a river. It was classified as subject to remediation according to Austrian law Alsag (Austrian law for abandoned hazardous sites) [27] in 1996. In 2000 it was categorized class 1, giving it the highest priority. During evaluation of the site, samples of 187 bores at different locations and depths were the general flow direction (south-east) was interfered by a nearby underground tube. Twenty-one extraction wells were drilled which would be regulated by control wells. Furthermore, three monitoring wells were drilled. All the mentioned bores are downstream of the site.

The objective of the pilot study was to assess options for a fullscale long-term plant, in order to be cost-effective while meeting all environmental obligations. The goal is to make recommendations on which treatment steps have to be implemented in a pumpand-treat system. Most of the treated groundwater will be recycled up-stream of the contaminated site through an infiltration gallery. However, part of the pumped water has to be discharged to ensure hydraulic containment. For discharge of the treated groundwater three different options were considered with increasingly stringent legal standards: (1) discharge into sewerage system, (2) discharge into the adjacent river, and (3) recharge into groundwater. Hence, the principal aims of the study were to (i) examine the performance of the physical and biological treatment steps, (ii) identify problems that occur during treatment plant operation and (iii) determine whether remediation goals may be achieved for discharge of effluent water into a sewer, surface water, or recharge into groundwater.

2. Methodology

21. Groundwater

Two of the mentioned bores exhibiting the highest contamination levels were selected for the pilot plant experiments, one located near the former tar disposal (Well 1), the other one at the former naphthalene scrubber (Well 2). The previous investigations about the groundwater were completed with additional analysis to get a complete picture of the groundwater quality of the two wells, since they differed significantly in composition. An overview of the quality of the groundwater is provided in Table 1. The groundwater had a stable temperature between 13.1 and 13.7 -C and a pH between 6.7 and 7.4 throughout the year.

The groundwater of both wells showed comparable COD concentrations of 21-68 mg/l. The other parameters showed differences, for example, Well 1 had higher concentrations of

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Table 1		
Groundwater quality	and analytical methods	
1	0	

Parameter	Method	Well 1	Well 2
pfi	DIN ² 38 404-5	67-74	7.1-7.2
Dissolved axygen (DO) (mg/l)	DIN EN ⁹ 25814	0.0	0.0
Oxidation reduction potential (ORP) (mV)	150° 11272	-280 to -380	-260 to -330
Conductivity (µS/cm)	DIN 38 404-8	1378-1424	1412-1437
PAH (µg/l)	DIN 38407 F8	182-745 ^d	789-865 ^d
Naphthalene (µg/I)	DIN 38407 F8	56-128	589-648
Benzo(a)pyrene (µg(1)	DIN 38407 F8	<0.03	<0.03
BTEX (µg/l)	DIN 38407/9-1 GC	295-635	742-805
Benzene (µg/l)	DIN 38407/9-1 GC	247-547	366-512
Phenois (mg/I)	DIN 38 409 H16 1-3	0.21-0.53*	0.04-0.08*
Cyanides (mg/l)	DIN 38405 D13	0.0-0.18	0.18-0.25
TDC(mg/l)	DIN EN 1484	4.32-13.0	6.0-6.4
COD (mg/l)	DIN 38409-H 41	21-61	37-68
BOD ₅ (mg/l)	DIN 38 409-H51	4.5-12.5	10.5-16.0
HC (mg/T)	EN ISO 9377-2	0.21-1.10	0.32-0.88
NH4" (mg/I)	DIN 38414	3.2-7.1	3.1-3.9
NO ₂ - (mg/l)	DIN 25777	<0.01	<0.01
NO ₃ - (mg/l)	DIN 38405	<0.01	<0.01
Fe ^{2*} (mg/l)	DIN 38406 E1-1	0.24-0.48	2.7-32
Min ^{2*} (mg/T)	DIN 38405-33	0.12-0.21	0.35-0.46
52 (mg/l)	DIN 38405 D 26	9.9-17.6	3.12-3.48
PO ₄ -P (mg/I)	DIN EN 1189	<0.05-0.12	0.05-0.13

^a DIN standard.

^b European standard.

E ISO standard. d Sum of EPA 16.

* See comments on phenol analytics in Section 3.2.5. [†] Easily purgeable cyanides.

hydrocarbons, phenols, and sulfur, while Well 2 had higher concentrations of PAHs and BTEX.

2.2. Pilot plant design

As described earlier, the pilot plant comprised several treatment steps. The general layout and principal processes of the pilot plant are presented in Fig. 1.

2.2.1. Sedimentation/flotation

The sedimentation/flotation was carried out in an open top rectangular basin of 18.10 m^3 volume (L \times W \times D: 4.6 m \times 2.3 m \times 2.5 m). It consisted of an influent zone, a settling zone, and a pump chamber separated by baffles. The HRT was 5 h during normal flow condition (11/s) and 2.5 h during high flow condition (21/s). It turned out that a significant part of the particles do not settle but rather float on the surface. To enhance separation by flotation, the influent zone was equipped with an aeration system after 64 days of operation. Two membrane disc diffuser (Nopon KKI 225: A= $2\times0.025\,m^2$) were installed, producing bubbles of 1–3 mm diameter. The air supply was 1.5–4.0 m³/h. Furthermore, a skimmer was installed to continuously remove floating particles while the settled solids were excavated manually on occasion.

2.2.2. Submerged fixed film reactors (SFFRs)

Two slightly different SFFRs, termed "BioH" and "BioK", were installed and operated as parallel systems to investigate different HRTs. BioH had a volume of 1.87 m³, BioK had a volume of 1.58 m³, hence different HRTs occurred (Table 2). At start-up, the reactors were inoculated using activated sludge. The inoculum was obtained from a waste water treatment plant at an oil refinery, adapted to the treatment of hydrocarbons.

The air supply for the reactors was 2 m³/h each. Since the level of dissolved oxygen (DO) in the effluent after 2 months of operation was very high at 9 mg/l, the air supply was reduced to $1.5 \text{ m}^3/\text{h}$. The residual DO of 7 mg/l was still sufficient for aerobic biological

Table 2 SFFR technical data

	BioH	Blok	
Height (m)	1.65	1.40	
Volume (m ³)	1.87	1.58	
Diameter (m)	1.20	1.20	
Height over all (m)	2.18	1.80	
Package material	LECA expanded clay pellets (diameter: 6-8 mm)		
Aeration Flow regime	Tube diffusers; m Co-current upflow	embrane area/reactor = 0.065 m ³ v of influent and air	
and the second se			

activity. The groundwater flow was split 50:50 to both SFFRs. The resulting HRT in the SFFRs were 1.04 and 0.88 h, respectively, at a flow rate of 1 l/s. Accordingly, at the high flow conditions of 2 l/s HRTs were 0.52 and 0.44 h in the SFFRs.

2.2.3. Multi-media filter (MMF)

The technical data of the MMF are summarized in Table 4. In between the SFFRs and the MMF was a storage tank. The pump therein produced the pressure to move the groundwater further on through the MMF (HRT = 0.63 or 0.32 h) and the following GACF (Table 3)

Table 3

echnical data of the multi-media filter (M	MMF)
--	------

Filter height (m) Filter volume (m ³) Diameter (m) Overall height (m)		1.40 2.3 1.09 1.94
Package material	Particle size (mm)	Layer and thickness (cm)
Hydro anthracite	0.6-1.6	Top: 40
Fine filter sand	0.7-1.3	Upper middle: 40
Coarse filter sand	2.0-3.15	Lower middle: 40
Gravel	55-8.0	Supportive layer: 20



Fig. 1. Scheme of the pilot plant setup. SED: sedimentation/flotation; BioH, BioK: submerged fixed film reactors (SFFR); GACF II; granulated activated carbon filters; MMF: multi-media filter; P1, P2: pumps.

Table 5

2.2.4. Granulated activated carbon filter (GACF)

Two similar GAC filters were employed to obtain data about the adsorption capacity of activated carbon. (GACF 1: 88 days, and GACF 2: 94 days). It was intended to operate them consecutively. However, due to the excellent effluent quality, only one of them was operated at a time whereas the other one was maintained in a stand-by mode. The volume of the GACFs was 1.5 m³ each, providing an HRT of 0.42 during standard flow rates and 0.21 h in the high flow state. The diameter of the filter was 1.2 m, sampling ports were at the beights of 1.7, 0.7 and 0.2 m. The carbon used in the GACF were in the form of pellets "Donaucarbon CC50P" (see Table 4).

Experimental stages of the pilot treatment plant

Stage	Time, Well
0: start-up	40 days, Well 1
1: standard hydraulic loading rate (flow rate 1 l/s), phosphate dosage	65 days, Well 1
 standard hydraulic loading rate (flow rate 1 l/s), without phosphate dosage 	30 days, Well 1
3: high flow (flow rate 2 Us)	55 days, Well 1 + Well 2

3. Results and discussion

3.1. Development of groundwater quality

2.3. Data collection, sampling, and analysis

The pilot plant was controlled by a programmable logic controller (PLC) and data about flow, pressure, temperature and pH were recorded automatically every hour. Samples were taken weekly from the influent, whether Well 1 or a mixture of Well 1 and Well 2 during the high flow stage. Samples were also taken from the process units, described above (SED, Bio, MMF and GACF). The parameters analyzed are listed in Table 1 along with the methods used for analysis.

2.4. Schedule of experiments

Experiments were conducted for 6 months, treating either 1 or 21/s with HRT all over the treatment steps of 7 and 3.5 h, respectively. The experimental stages were as shown in Table 5.

Table 4

Supplier data of activated carbon	"Donaucarbon CC50P"
-----------------------------------	---------------------

Pellet diameter (mm)	35.40	
Mean density (kg/m ²)	500±50	
Ash content (%, w/w)	<15	
Water content (X, w/w)	<5	
lodine absorption (mg/g)	>800	
CICe-activity (%, w/w)	>40	

In the course of the operation of the pilot plant the concentration of the contaminants showed significant variations in the influent. Fig. 2 shows the development of the COD concentration as a gross parameter of organic compounds and sum of 16 EPA priority pollutant PAHs as one of the main treatment goals. As a general tendency, the COD concentration and all other contaminants decreased slightly during stage 1 while the pump was in charge





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with minor bounce back effects, when the pumping was suspended for a few days. This is a typical trend also witnessed in other experiments [28]. In stage 3 Well 1 and Well 2 each contribute 50% to the influent; the generally higher concentration of contaminants of Well 2 increased the COD and also the concentration of the other compounds.

3.1.1. General performance of the plant

After the inoculation, sufficient time was provided for the establishment of an appropriate biological activity in the SFFRs. Within the first 40 days, their pressure in the SFFRs increased slightly, indicating biofilm growth. At this time a back flush of the biofilters was performed but the pressure conditions did not change much. Thereafter the pressure was stable throughout the whole duration of the experiment. This date was considered as the end of start-up and the beginning of the test phase. The removal rates of the two different sized SFFRs were marginally different, with BioH offering a higher HRT showing a subtly better performance. But the satisfactory effluent quality in stage 3, at high hydraulic loading, showed that the biological degradation had further capacity. The groundwater, coming in almost clear at a very low redox potential (ORP) in the range of -260 to -380 mV, turned out to be a difficult matrix. At contact with air in the first process step the turbidity increased greatly and the groundwater became grayishwhite. The main reason was the formation of elemental sulfur, but iron and lime precipitates were formed as well and tar like components were observed. A thick grayish floating layer was formed on the sedimentation tank after a few weeks of operation.

The potential chemical mechanism behind the formation of sulfur is a coproportionation between sulfite and sulphide (Eq. (1)). An elementary analysis of the flotate (HEKAtech, CHNSO Analyzer) werified the high content of sulfur, 43.6–74.7% of dry mass, while the carbon content was only 5.4–9.8%.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$
 (1)

In the process steps following sedimentation/flotation the turbidity decreased due to particle removal by mechanical filter effects (Fig. 3). Still, turbidity values after the MMF were remarkably high, higher than the turbidity levels usually expected after multi-media filtration.

A back flush of the MMF was done every 2 weeks in stages 1 and 2, in the high flow stage every 3–6 days. The back flush conditions were 2 min air upflow (40 m³/h) and 5 min water upflow (32 m³/h).

Probably due to the elevated particle concentration after the MMF the pressure drop in the final GACF I increased relatively quickly (80–120 mbar per week) and it had to be substituted by the second GACF II for stage 3.

Clogging effects by sulfur or iron are also reported by other authors when treating groundwater [29]. Over time, the precipitates described herein caused constrictions in pipes and clogging of pumps and they disturbed measurement devices, including flow meters and pH and oxygen sensors. This influenced the stability of the control mechanism for flow regulation and bouncing of the flow rate aroused. The flow fluctuations gradually worsened until a cleaning of the affected pipes and flow sensors was made in stage 2 and the plant returned to good operating conditions. In stage 3 the hydraulic capacity of the pilot plant was close to its limits and a couple of plant shut downs occurred due to different technical failures. Despite the mentioned problems, it has to be noted that the plant



Fig. 4. The removal of COO, HC-index, EPA-PAHs and BTEX. All three stages are shown with an average value for each process step (influent, sedimentation, submerged fixed film reactors, multi-media filter, and granulated activated carbon), bars indicate minimum and maximum values.

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3-5

Qualitative and o	quantitative analyzes of sedi	imentation exhaust air		
Retention time (min)	Substance	Qualifier for identification (%)	Off gas concentration stage 1/2 (ppm)	Off gas concentration stage 1/2 (ppm)
9.7	Benzene	95	190-260	370-500
14.5	Ethylbergene	91	16-34	32-66
12.3	Toluene	91	12-17	23-32
14.7	olm-Xylene	91	9-13	16-25
15.3	p-Xylene	90	6-7	12-14
10.3	Naphthalene	23*	5-7	10-13
18.7	Indane	94	5-7	10-13
12.6	Not identified	-	5-7	10-13
17.7	Mark Islamilitiand		3.5	7 10

² Unsatisfactory identification.

Isopropyibenzene

Ethylcyclohexane

was operated constantly almost throughout the whole investigated period. After 6 months of continuous experiments the SFFRs were opened and the carrier material was inspected. Only in the very bottom layer of the carrier material some deposits of tar components were found. With this regard, the choice of smaller carriers seems not advisable. Smaller carriers provide a higher surface to volume ratio and increased biofilm densities. While the volumetric conversion rate might be enhanced by using smaller size carriers, the filters can also become more prone to clogging.

94 49'

3.2. Removal of organic contaminants

3.2.1. COD

COD is a gross parameter for total organics. The decrease along the course of flow through the plant provides an overview of the performance of the different process steps. Fig. 4 shows that each process step contribute to the removal of COD. The decrease in the sedimentation basin is obviously due to removed sediments and floating particles but the long HRT and the aeration also might allow some biological degradation in this step. The SFFRs fulfilled their expectations quite well and the MMF contributed by retaining eluted biofilm particles and other suspended solids. However, the data also show that a significant percentage of the COD is not eliminated. A residual concentration between 9 and 15 mg/l neither was biodegraded nor absorbed on the activated carbon. Additional analyses of the BOD₅ proved that the organics, which are readily biodegradable, were removed between 95 and 99%. Influent BOD₅ concentrations between 16.0 and 4.5 mg/l (average 10.5 mg/l) were degraded to 0.8 and 0.1 mg/l (average 0.4 mg/l). A comparison with the MCP site Griftpark [23] shows, that their influent COD of 115 mg/l is almost twice as high as the maximum COD influent of this site (61 mg/l), on the other hand the average removal efficiencies herein are slightly better than their achievements (42–50%), even the HRT at Griftpark plants is twice as long.

7-10

4-11

Mass-fraction 58.0-78.0 Ø 61.4% 4.8-10.0 Ø 8.8% 3.5-5.0 Ø 4.6% 1.8-22.0 Ø 4.6% 1.5-2.0 Ø 1.6% 1.5-2.0 Ø 1.6% 1.5-2.0 Ø 1.6% 1.0-15.0 Ø 1.3%

10-150178

05-1501.0%

3.2.2. HC-Index

The HC-index measures the sum of hydrocarbons which are a major target of purification efforts. The results shown in Fig. 4 indicate that the SFFRs achieve significant removal of contaminants. Even during the high flow stage the residual HC concentration is below 0.1 mg/l. This reconfirms the good biodegradability of the hydrocarbons. The following MMF does not contribute much, but the GACF absorbs the residual HC below detection limit (0.03 mg/l). Oesterholt et al. confirm the good bioavailability of hydrocarbons. Mineral oil concentrations of even 9.5 mg/l get degraded to 94% (HRT - 2 h) [23].

3.2.3. EPA-PAHs

er The analysis for aromatic compounds focused on the 16 EPA al priority pollutant PAHs, representative for a class of carcinogenic



Fig. 5. Distribution of PAHs in influent (Well 1 + Well 2, 1:1) and in effluent.

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15.9

13.8

and mutagenic substances. PAHs of higher molecular weight are more toxic, but the lower molecular weight compounds are more soluble in the groundwater and thus have a greater potential to reach receptors [18]. The transport of PAHs is complex, since it not only depends on water solubility, but these compounds can also be transported as colloids or adsorbed to humic acids [30]. Two or three ring PAHs are biodegraded readily while compounds containing more than four rings, are biodegraded cometabolically, with other compounds acting as growth substrates [31]. Low solubility of complex PAHs reduces their bioavailability and makes biodegradation difficult resulting in their persistence in contaminated sites [32].

In the investigated case the concentration of PAHs in groundwater with a higher ring number than four were below or close to the detection limit (0.03 µg/l). The distribution pattern of PAHs in Well 1 and Well 2 were significantly different. In Well 1 (561 µg/l EPA-PAHs) located close to the tar disposal site, 49% of the PAH content was acenaphthene. In Well 2 (1692 µg/l EPA-PAHs), located near the former naphthalene scrubber, 75% of the PAHs was naphthalene. Similar to the other hydrocarbons, PAH concentrations were highest immediately after implementing a new well and exhausted while the wells were pumped.

Both influent qualities could be treated successfully in the SFFRs with removal rates between 77 and 98%, Fig. 5 gives an example of the distribution of PAHs in the inlet and the outlet of the SFFR. Naphthalene, being the smallest PAH, proved to be 100% available for biodegradation. Acenaphthene was slightly more persistent, which lead to a relatively higher share in the PAHs present in the effluent. Residual concentrations of PAHs were almost completely adsorbed in the subsequent activated carbon treatment. Including the GACF the removal rate in all stages was beyond 99.5% with total levels in the range from 0.27 to 0.88 µg/L These results are confirmed by other authors. Findings in Griftpark show comparable influent concentrations and removal rates [22], while Guerin [12] treats a much higher concentration (total PAH- 120 mg/l) successfully with 99.8% removal, at a HRT of 3.5 h [4].

In previous experiments in a similar application [33] it was demonstrated that PAHs are not only adsorbed in the GACF but also undergo microbial degradation. The occurrence of aerobic biological activity is supported by the observed oxygen consumption in the GACF. By this effect, termed bioregeneration, the lifetime of a GAC filter can be extended and the activated carbon require less frequent regeneration [34,35]. At the end of the experiments from both GAC filters several samples of the activated carbon at different filling levels were taken and the residual iodine adsorption capacity was determined. From these analyses and the total volume of groundwater treated in each GACF, the maximum treatment capacity of the activated carbon was calculated. For both filters, a similar capacity of 24,000 m³ groundwater per m³ activated carbon was determined.

3.2.4. BTEX

BTEX are highly volatile toxicants, corresponding to their higher Henry's law constant compared to other hydrocarbons [36] and get easily stripped by aeration [22]. Therefore most of the BTEX were removed in the aerated sedimentation/flotation unit. In order to verify this, the sedimentation and the SFFRs were sealed and the exhaust air was analyzed by gas chromatography (GC). A flame ionization detector (FID) was used for the exhaust air analysis, Organic carbon was found in the range of 96.3% (stage 1 + stage 2) and 95.6% (stage 3) of the organic carbon represented by BTEX in the influent water. A quantitative analysis using a sequential purge-and-trap analysis with MS detector proved, that these organic exhaust gases consisted mainly of BTEX, with a benzene concentration of >58%, while other substances as, e.g. naphthalene were not much present.

Smple	(jug(j)	(hg/l)	e-Cresol (Jug/I)	p-Cresol (ju gft)	2-Ethyl- phenol (µa/1)	2,6- Dimethyl- phenol (µg/l)	2,5- Dimethyl- phenol (µg/l)	2.4- Dimethyl- phe nol (µg/l)	3.5- Dimethyl- phe nol+4- phe nol (µgl1)	2.3- Dimethyl- phe nol (µg/l)	3.4- Dimethyl- phe nol (µg/l)	2,3,5- Trimethyl- phe nol (µtg/l)	2,4,5- Trimethyl- phe nol (µt,0)	3,4,5- Trimethyl- phe nol (µg/l)	2- 1 opropyl- phe nol (µg/l)	4- 1 spropy(- phe nol (µtf/l)
Mell 1 influent	296.1	<0.5	56	42	<05	5.5	20.9	55.0	65,1	25.1	28,3	12.5	8,8	2.2	8.1	39.3
EDefluent	2650	6.7	40.5	227	53	10.2	16.3	50.3	50.3	20,6	10.1	13	12.1	1,8	1.7	11.9
SFFR BioH e filtuent	184.8	7.9	205	11.9	3.1	6.7	10.6	26,0	42.9	14.4	7.6	8.9	8,0	1.3	0.7	11.9
SFIR BloKemuent	232.1	8,3	31.5	180	4.1	6,8	13,4	32.0	51.1	17.6	9,1	30.8	2.6	1.6	1.4	12.0
CACFemant	72	40.5	*05	3	*0.5	40.5	40.5	40.5	0.9	A.5	40.5	-0.5	20.5	A.5	40.5	40'S

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The identified substances listed in Table 6 comprise more than 90% of the total organic C present in the off gas. The GC-MS analyses brought not only a satisfactory identification of the substances, but also quantitative data, which fit very well to the TOC balance. The results proved that BTEX are almost completely removed by stripping and no biological degradation was observed. While no exhaust air treatment was installed at the pilot plant, a major plant would certainly require one to trap BTEX. Adsorption on activated carbon is probably the most convenient technology. Other studies [4,23] show very promising results for biological removal of BTEX.

3.2.5. Phenols

Phenols were analyzed according to DIN 38 409 where three different methods are described: method H16-1 employing extraction of phenols with an organic solvent, H16-2 consisting of a distillation and an extraction step, and H16-3 done by distillation only. The results of these three methods were significantly different (e.g. for a sample from Well 1: 0.48, 1.05, and 0.65 mg/l). The reasons might be the interference of certain contaminants to the color reactions on the one hand; on the other hand the cracking of larger molecules with hydroxyl groups during distillation, which are later detected as phenols. To clarify the picture, samples were sent to the Geoscience Center Goettingen, Germany, a university laboratory specialized in phenol analytics. Their detailed results proved that the sum concentration of phenolic compounds of both Well 1 and Well 2 were around 300-500 µg/l and they were reduced to 5-10 µg/l in the GACF effluent, This is in accordance with other findings [22]. While the concentration of phenol itself is low, several other compounds have higher concentrations (Table 7). Substances with concentrations <5 µg/l (e.g. m-cresol) are excluded of the table. Therefore, phenols can be considered an uncritical parameter in this groundwater

3.3. Removal of other contaminants

The concentration of total cyanides found in the influent was 0.5–0.7 mg/l. Total cyanides proved to be inert and no significant degradation was observed in the process steps. Also on other sites, cyanide appeared not to be accessible for any treatment, since it is present in complexes [22]. The reason is that cyanide compounds found at former MGP sites mainly occur as relatively nontoxic iron-complexed forms, such as ferric ferrocyanide, rather than the highly toxic free cyanide forms. The determination of cyanides in MGP site

Table 8

Summary of the effluent parameters, compared to Austrian legal requirements

cleanup is due to misunderstanding, that not all chemical forms of cyanide are highly toxic, e.g. ferric ferrocyanide, also known as Prussian blue, is a widely used coloring agent of low toxicity [37]. Moreover, the chemical conditions at most former MGP sites limit the extent to which free cyanide may be released into air and water from complex cyanides [38]. According to Shifrin et al., there is little, if any concern for either ingestion or dermal contact exposures to any form of cyanide potentially present in soil at former MGP sites [38].

The Austrian legal requirements for discharge into water bodies have no regulation for total cyanides, but easily purgeable (-free) cyanides are limited with less than 0.1 mg/l. This requirement could be achieved with effluent concentrations mostly below the detection limit (0.01 mg/l).

Ammonium was found in concentrations between 3.1 and 7.2 mg/l, while oxidized N components were not present. Part of ammonium was consumed during biological conversion of the organic compounds but still more than 50% of the ammonia was left in the effluent. Nitrification in the SFFRs was not observed or only to a very small extent, probably due to the low temperature and the low HKT.

Sulfide was detected in significant concentrations in the range of 3.1–17.6 mg/l. The actual concentration in the groundwater was presumably even higher but at contact with air, sulfide was rapidly oxidized and the concentration in the effluent was very low (<0.08 mg/l).

Heavy metal ions were analyzed only monthly, since their concentrations were insignificant, far below the treatment requirements.

3.4. Comparison of the performance in the different stages of investigation

In stage 1 the effluent quality met all expectations, in particular the limits of direct discharge into open water bodies. The quality came even close to the very stringent standards set within the Austrian Groundwater Quality Monitoring Ordinance, which are established to guard groundwater resources that are a major source of drinking water in Austria (Table 8). Usually such high standards can be only achieved involving advanced treatment technologies such as ozonation or UV/peroxide treatment.

In stage 2 the necessity for phosphorous supplementation should be clarified, Nutrients are essential for efficient degradation

Parameter	Disposal into sewerage system	Disposal into public water bodies	Groundwater threshold value ordinance	Effluent stages 1 and 2 (average)	Effluent stage 3 (average)
PAH	-	100 µgn (16-EPA*)	0.1 µg/I (6-PMH ^b)	0.27 µg/1 (16-EPA)	0.88 µg/1 (16-EPA)
Benzene	-	-	0.1 µg/l	<0.1 µg/l	<0.1 µg/l
BTEX	100 µg/1	100 µg/1	Limited for benzene and toluene; 0.1 µgfl each	<0.1 µgn	11.4-34.0 µg/l
Phenois	20 mg/l	0.1 mg/1	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	<0.01 mg/l ^p	0.76 mg/F
Cyanides (easily purgeable)	0.5 mg/1	0.1 mg/1	0.03 mg/l (total cyanides)	±0.05 mg/1	0.22 mg/1
TOC		25 mg/1	1. The second	3.6-5.8 mg/l	6.4-8.7 mg/l
000	11-11	75 mg/1	-	8.1-13.4 mg/l	13.9-24.1 mg/l
HC	20 mg/l	10 mg/l	0.06 mg/1	<0.1 mg/l	<0.1 mg/l
NH4-N	-	10 mg/l	0.03 mg/1	4.6-7.5 mg/1	6.2-9.5 mg/l
NO ₂ -N			0.01 mg/1	0.0-0.5 mg/l	0.0-0.1 mg/1
Fe				0.22-0.34 mg1	0.42-0.55 mg/1
Mn	10 mg/1	1.0 mg/1		0.18-0.20 mg/l	0.22-0.23 mg/1
51	14110	2.0 mg/l	-	<0.08 mg/1	<0.08 mg/l

^a Sum of benzo(a)pyrene, fluoranthene, benzo-(b)-flouranthene, benzo-(k)-flouranthene, benzo-(ghi)-perylene, inden-(1,2,3-cd)-pyrene.

^b Sum of 16 PAH congeneres according to EPA.

⁶ HS-SPME-GC-MS according to a new DIN-method, which is under way

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of organic HC compounds. As a general rule, in aerobic degradation the optimum relation of COD:N:P is estimated by 200:5:1. A maximum of about 61 mg/l COD therefore needed 1.5 mg/l N and 0.3 mg/l P. Such, the concentration of 5(±2) mg/l NH4-N was more than sufficient. This was not the case for phosphorous. Since the detected phosphorus-levels were only around 0.05 mg/l, phosphorus was added in the form of diluted phosphoric acid by membrane pump. A concentration of 0.5 mg/l P was set, in order to clearly avoid a P-limitation. On the other hand, remaining P might also cause problems, e.g. pond treatment as a final polishing step was considered where elevated P levels might stimulate algal growth. As well it was suspected that remaining P might enhance biological activity in the soil after re-infiltration, which would then lead to problems due to clogging of infiltration wells. Therefore the addition of P was seen ambivalent. To investigate the requirement for P supplementation, the second experiment stage was conducted without the addition of phosphorus. The removal results for core contaminants were similar and no significant loss of performance was observed. It was concluded that phosphorus was not a limiting factor in this case. One reason was, that approximately 50% of the organic contaminants were removed by physical process steps (sedimentation, flotation, stripping, and filters). Therefore the addition of phosphorus was not resumed. However, such a decision should not be taken easily and not only the concentrations of pollution but also the remediation concept has to be considered

In the final experimental stage (stage 3) the hydraulic load was doubled to check the limits of plant performance. As it can be taken from Table 1, under these conditions the effluent quality did not meet all criteria for discharge into open water bodies but it was still sufficient for disposal into the sewage system.

4. Conclusions and recommendations

The investigated pilot plant setup provided valuable field experience for a full-scale plant. At a flow rate of 1 l/s high effluent quality could be achieved, meeting the Austrian legal requirements for discharge into public water bodies, which was a main treatment goal. At double flow rate the effluent quality worsened. Still the requirements for discharge into public water bodies were achieved except for the cyanide concentration. Appropriate pre-treatment turned out to be a critical issue to achieve good results and to maintain stable operating conditions. The first treatment step should have a sturdy construction, which can be easily maintained, and it should allow simple removal of floatable or settleable precipitates. A HRT >3h is recommended to provide sufficient time for completion of precipitation reactions in order to protect the following reactors from clogging.

The selection of the reactor configuration for biological treatment is a critical point. Exhaust air treatment, filling material and backwashing have to be considered. The chosen system turned out to be highly reliable and the SFFRs contributed much to the degradation of the typical MGP contaminants. As another recommendation, it is suggested for the full-scale plant to establish a counter-current flow regime instead of the applied co-current flow. This would leave tar precipitations at the top layer where they can be easily removed. Furthermore the aeration devices at the bottom would not be affected by deposits as observed in the pilot plant.

The addition of phosphate showed no clear evidence of improved biological removal of contaminants, even while the COD:N:P ratio might suggest so. However, as discussed before, the necessity of nutrient dosage should be assessed in each individual case

The MMF exhibited a certain deficit in protecting the GACF from particles from the SFFRs. The reason is presumably the breakthrough of finely dispersed sulfur precipitates through the MMF. With regard to the observed pressure increase also the GACF should be equipped with a back flush option. Nevertheless, the final GACF fully assured the effluent quality and the residual concentrations of the target contaminants were close to detection level.

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In summary the investigated pump-and-treat system proved to be an efficient and cost-effective means of hydraulic containment and groundwater protection. This concept as presented above is currently implemented in the design of a full-scale treatment plant.

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Ammonium Removal from Anaerobic Digester Effluent by Ion Exchange

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Abstract The effluent of a 500 kW biogas plant is treated with a solid separation, a micro filtration and a reverse osmosis to achieve nutrient recovery and an effluent quality which should meet disposal quality into public water bodies. After the reverse osmosis, the ammonium concentration is still high (NH₄-N = 467 mg/l), amongst other cations (K⁺ = 85 mg/l; Na⁺ = 67 mg/l; Mg²⁺ = 0.74 mg/l; Ca²⁺ = 1.79 mg/l). The aim of this study was to remove this ammonium by ion exchange. Acidic gel cation exchange resins and clinoptilolite were tested in column experiments to evaluate their capacity, flow rates and pH. Amberjet 1500 H was the most efficient resin, 57 BV of the substrate could be treated, 1.97 mol NH₄-N/l resin were removed. The ammonium removal was more than 99 % and the quality of the effluent was very satisfactory (NH₄-N < 2 mg/l). The breakthrough of the observed parameters happened suddenly, the order was sodium – pH – ammonium – potassium. The sharp increase of the pH facilitates the online control, while the change in conductivity is less significant. A regeneration with 3 bed volumes of 2 M HCl recovered 91.7 % of the original cation exchange capacity.

Keywords Ammonium; Anaerobic Digester Effluent; Clinoptilolite; Ion Exchange

INTRODUCTION

Biogas has become an increasingly important source of alternative energy in Austria. While 119 biogas plants were operated by the end of 2003 the number almost doubled to 231 by the end of 2005 (Energiecontrol, 2006). Not only the number, but also the size of the plants increased, leading to massive amounts of digester effluent, being still rich in organics and also in nutrients. The concentrations of nitrogen, mainly present in the form of ammonia, can be more than 100fold higher than in municipal waste water. The disposal of these residues has become the bottle neck of this sustainable energy source. Traditionally the digestate was used for manuring. However, due to the legal limits for N-fertilization per area of farmland (DüngemittelVO, 1994 - Austrian Law for Fertilizer Output), imposed to protect the

groundwater, increasingly big areas are required and rising transport costs would emerge. An alternative option is to separate the solid residues from the liquid fraction that contains the mayor amount of the nitrogen. The less voluminous solids are again used for fertilizing whereas the liquid fraction has to undergo further treatment. Nitrogen in water bodies promotes eutrophication (Thornton et al., 2007), ammonium causes oxygen demand Weatherley, (Jorgensen and 2003). Ammonia toxicity to fish and other aquatic significant animals is very and concentrations in the range 0.2-0.5 mg/l can be fatal (Wiesmann, 1994). Hence, the removal of ammonium from effluents is of great importance in the control of nitrogen pollution (Wen et al., 2006] and increasingly strict legal limits have been implemented. The traditional way for nitrogen removal

from wastewater or liquid wastes is the biological process of nitrification/denitrification. (Kelly, 1996; Karadag et al., 2006). But the high ammonium concentrations in anaerobic digester effluent may be inhibitory to the biological process and also shock loads can cause trouble to biological treatment systems. Therefore, current research focuses on physical nitrogen removal methods as economically and environmentally friendly treatment alternative.

At the biogas plant investigated herein, a treatment setup consisting of a solid separation, a micro filtration and a reverse osmosis (RO) was implemented. One goal of this treatment process is the recovery of Phosphorus, nitrogen nutrients. and potassium should be extracted in a way, that it can be directly used for manuring or allows the production of a fertilizer. The second goal is the purification up to an effluent quality which meets the requirements for internal usages such as process water, irrigation on farmland or even disposal into public water bodies. In this context, anaerobic digester effluent proved to be a challenging substrate for purification (Novak et al., 2003), especially the ammonium concentration was still too high after RO treatment.

The scope of this study was to evaluate the efficiency of an ion exchange unit for final ammonium removal to meet the required limits. Within the last decades, much research has been done about the cation exchange capability of zeolite, a naturally occurring alumino silicate. Among these, clinoptilolite is considered most suitable for ammonium exchange regarding selectivity and capacity (Thornton et al., 2007). Therefore clinoptilolite was compared to polymeric ion exchange resins, since they have higher cation exchange capacity, higher reaction rates and chemical resistivity (Farkas et al., 2005).

METHODS

Origin of the Substrate (RO Permeate)

A 500 kW biogas plant in Austria is operated in co-digestion mode with cow manure (50 %), kitchen and bio waste (25 %), slaughter waste (15%), and energy crops (10 %) as a substrate. The plant produces approximately 3 m³ effluent per hour. Solids are separated with a screw press (mesh size = 1 mm) and a vibration sieve (mesh size =0.25 mm). This pre-treatment is followed by submerged micro filtration (MF; a Mitsubishi, pore size = $0.5 \mu m$) and a twostage reverse osmosis (RO) for sea water desalination (Filmtec SW 30 HR 380), producing 2 m³ RO permeate per hour (Figure 1). This treatment of residues shows high reduction rates for all parameters. The micro filtration completely removes the suspended solids and most of the colloids. Therefore the COD is largely cut down in this process step. Naturally MF does not change the ammonium concentration, but it gets significantly reduced subsequently in the RO. Nevertheless, the RO effluent is still very high. This was on the one hand due to the very high inflow concentration (NH4-N > 5,000 mg/l), on the other hand, because the treatment of anaerobic digester residuals is a fairly new topic, and the pilot plant herein was facing operational problems several times. To evaluate the capacity of the ion exchange resins, challenging conditions were applied and the experiments were conducted with a ammonium concentration of NH4-N = $467.4 \pm 33.2 \text{ mg/l}$ (Table 1). This concentration is significantly higher than in comparable investigations with simulated municipal wastewater, in which NH4-N ranged from 19-176 mg/l (Leakovic et al., 2000; Jorgensen and Weatherley, 2003; Weatherley and Miladinovic, 2004). Ion exchange, as a further process step of the effluent treatment, should help to fulfill the requirements for internal use or disposal into public water bodies.



Figure 1. Setup for the treatment of the anaerobic digester effluent

	TS [%]	TN [mg/l]	NH4-N [mg/l]	COD [mg/l]	P [mg/l]	K [mg/l]
Digester Effluent	5.05	9,326	7,194	54,460	1382.00	2,344
MF Influent	4.95	8,818	6,640	47,870	1365.46	2,971
MF Retentate	5.39	9,521	6,748	59,690	1414.55	2,100
MF Filtrate	1.04	5,406	5,279	2,264	3.23	2,205
RO Concentrate	2.71	10,697	10,484	15,968	17.67	4,456
RO Permeate	0.00	482	467	95	1.07	85

Table 1. Average concentrations of various determinants in digestate treatment steps

Table 2. Concentration of cations and other parameters of interest in the RO permeate

pH	NH ₄ -N [mg/l]	K ⁺ [mg/l]	Na ⁺ [mg/l]	Mg ²⁺ [mg/l]	Ca ²⁺ [mg/l]	Alkalinity [mg/l]
8.05 ±- 0.07	467.4 ± 33.2	85.0 ± 6.2	66.5 ± 4.1	0.74 ± 0.18	1.79 ± 0.21	$3,400 \pm 100$

Description of the ion exchange process and investigations

Set up. The experiments conducted addressed several aspects: in a first approach, for all ion exchange materials the cation exchange capacity (CEC) in particular for ammonium was investigated. The further experiments then focused on the most efficient ion exchanger material:

- The impact of a feed solution with a decreased pH was evaluated
- The flow rate was tripled, therefore the contact time significantly reduced
- The necessary amount of acid for regeneration was specified

During these experiments, the sustainability of the CEC was observed, whether an

exhaustion of the absorption capacity could be observed.

For the experiments, glass columns of an internal diameter of 1.3 cm and height of 40 cm were employed and loaded with ion exchanger beads or clinoptilolite. **Table 3** summarizes the characteristics of the applied ion exchange materials. The beds had a volume of 20 cm³ and a height of 15 cm. The liquid was pumped through the columns with a peristaltic pump (Kouril PCD 83.2) in the down flow mode at a volumetric flow rate of 100 ml/h, which is equivalent to 5 bed volumes (BV) per hour, and a surface hydraulic loading of 1.26 cm³/cm²/min, which complies to an empty bed contact

time (EBCT) of 12 min. The EBCT and the flow rate of 1.26 cm/min applied herein are in a common range (McVeigh and Weatherley, 1999; Leakovic et al., 2000). Samples were collected automatically every 12 min (Auto Sampler FCC 61). The experiments had a duration of 15 h.

Applied resins, Activation and Regeneration. For the experiments, commercially available resins were chosen according to previous experience and recommendations of the leading producers (Rohm and Haas, Lanxess). As further material natural clinoptilolite from Slovakia was used.

Name	Exchanger Type	Matrix	Functional Group	Mean Size
Amberjet 1500 H	Strongly acidic Cation	Styrene divinylbenzene copolymer	Sulfonic acid	$650\pm50\mu m$
Amberlite 252 H	Strongly acidic Cation	Styrene divinylbenzene copolymer	Sulfonic acid	600 – 800 µm
Lewatit S100	Strongly acidic Cation	Styrene divinylbenzene copolymer	Sulfonic acid	$600\pm50\mu m$
Clinoptilolite	Slovakian natural zeolite	$Na^{+} Al_{6}Si_{30}O_{72}$	Crystall channels	63 - 315 µm

The activation of ion exchangers can be critical for the selectivity and ammonium exchange capacity (Hedström, 2001). As standard conditions, the dry resins and clinoptilolite were swelled with sodium chloride solution (5 % NaCl) for 24 h at room temperature. For activation the resins were fed with 20 BV sodium hydroxide (1M NaOH), afterwards with 20 BV hydrochloric acid (2M HCl). This flushing procedure is not only replacing cations with Na⁺ and subsequently with H⁺, but it is also cleaning and swelling the resins. The standard regeneration was accomplished with 10 BV of 2M HCl. For activation and regeneration the same flow rate was applied than during the ion exchange experiments (flow rate = 1.26 cm/min).

Analytics

The cations were determined with atomic adsorption spectrometry (SpectrAA 220, Varian Inc). Analyses of all other parameters were done according to standard methods for the examination of water and waste water (APHA, AWWA and WEF). Conductivity and pH were measured with a multiparameter instrument (340i, WTW). The experiments were performed at 20°C. Chemicals used were of analytical grade. The 50 % breakthrough of cations was determined graphically (**Figure 2**).



Figure 2. Observed parameters and graphical determination of the 50 % breakthrough of eg pH (with ion exchange resin Lewatit S 100)

Investigated Parameters. All parameters are reported as relative values (C/C0), except pH and conductivity. Typically, as shown in Figure 2 a sharp increase of pH, Na+, NH4-N and K+ occurred, while the increase of conductivity was less significant. Also Mg2+ and Ca2+ showed no clear breakthrough, minor fluctuations were due to longer hydraulic retention times, when the sample collector was changed. Since the concentrations of Mg2+ and Ca2+ were relatively small, and these cations and as well the conductivity had no clear correlation to the ammonium removal, these three parameters are not displayed in the further graphs. Also in the experiments of Dimova et al. (1999) a comparable water hardness showed no significant affect. The observed order of the cation elution corresponds to the affinity to the ion exchange material, the weaker the affinity of a certain group of ions, the sooner they get eluted.

RESULTS AND DISCUSSION

Comparison of Cation Exchange Capacities of different Resins

polymeric The exchangers generally exhibited a higher CEC and a more pronounced ion breakthrough, compared to clinoptilolite. Generally, the removal of cations was very efficient with removal rates for ammonia > 99 %. Amberjet 1500 H the best exchange capacity, exhibits followed by Lewatit S 100 and Amberlite 252 H (Table 4, Figure 3). Similar experiments with the side stream effluent of a fertilizer factory (NH4-N = 176 mg/l) provided comparable results with CECs for Lewatit S 4428 from 1.9 meq/ml to 2.8 meq/ml (Leakovic et al., 2000). The CECs achieved in the experiments reported here exceeded the producer data slightly, because presumably the total cation concentration applied was relatively high. The total exchange capacity includes not only ammonium, but also other ions competing for exchange (Chen et al., 2002). The strongest affect has K+ because of its higher affinity to the exchanger (Farkas et al., 2005). Similar results are reported by Wang et al. (2006) who tested the influence of several cations on ammonium removal. The low mobility of K+ was also observed in the experiments conducted here. The concentration exhibits a slow increase and reaches the initial concentration about 20 BV later than sodium. An effluent concentration of sodium, higher than the influent concentration, also suggests, that potassium with its higher affinity replaces already adsorbed sodium. Generally the adsorption of ions other than ammonium is significant and therefore will reduce the effective uptake capacity for ammonia ion and thus the economics of the process.

Beside cations, also organic contaminants are considered to reduce the ammonium uptake, as experienced in other studies (Farkas et al., 2005). Even though the substrate used for these experiments is a colorless liquid after treatment by reverse osmosis, there is still a COD of 95 +/- 12 mg/l, due to small organic molecules, which might have a negative impact on the CEC.



Figure 3. Typical experiment results of Amberjet 1500 H, Amberlite 252 H, Lewatit S100 and Clinoptilolite
Clinoptilolite has been found very effective for removing ammonia (Karadag et al., 2006), since it has a high affinity towards monovalent cations (Vokacova et al., 1986; Farkas et al., 2005; Wang et al., 2007). Still the CEC of clinoptilolite obtained in these experiments is significantly lower than for artificial resins with 0.97 meq/ml. Literature data mentions CEC values for clinoptilolite in a wide range from 0.05 - 1.15 meq/ml (Thornton et al., 2007). Generally an exchange capacity of only 20 - 25 % compared to strong acidic cation exchangers is predicted (Vokacova et al., 1986). With view on that, the performance of the clinoptilolite used herein is significantly above average.

Resin	Unit	Amberjet 1500 H	Lewatit S 100	Amberlite 252 H	Clinoptilolite
Cation Exchange Capacity	[meq/ml]	2.28	2.03	1.89	0.97
Capacity according to product information	[meq/ml]	> 2.0	> 2.0	> 1.7	-
NH ₄ -N exchange capacity [meq/ml]	[meq/ml]	1.97	1.76	1.64	0.84

Table 4. Ammonium exchange capacity of the tested resins

Order of ion breakthrough

Most studies concerning cation preference were focusing on bivalent ions, while experiments on monovalent ions are not so common. Standard works about polymeric strong acidic cation exchangers (Helferich, 1959; Inczédy, 1964) suggest an affinity order of $H^+ < Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$. Monovalent ions have weaker affinities than bivalent ions. Within the bivalents ions it generally applies, the smaller the cations, the stronger the affinities. In these experiments for Lewatit S 100 the sequence was $H^+ < Na^+ < NH_4^+ < K^+$, which is in accordance with the order mentioned above. Amberjet 1500 H and Amberlite 252 H have a different breakthrough order. The pH is the second parameter to increase after the sodium concentration. The increase of pH shows the exhaust of the protons as exchange ions, hence in that case sodium has a lower affinity to the ion exchangers than protons and the order of affinity was $Na^{+} < H^{+} < NH_{4}^{+} < K^{+}$.

Amberlite 252 H exhibits the fastest ion breakthroughs in all experiments, the slope of the observed parameters increases almost twice as fast as for Amberjet 1500 H. For Lewatit S 100, all parameters increase with similar slope, while for Amberjet 1500 H and Amberlite 252 H the increase of potassium is significantly more gentle. The reason for that is presumably that potassium with its higher affinity partly substitutes other cations.

For clinoptilolite, the increase of all parameters is significantly less steep. This reconfirms, that clinoptilolite needs a longer contact time of 15 - 60 min to reach equilibrium, depending on the ammonium concentration, as stated by Thornton et al. (2007) and that the current flow rates are too high for a full exchange. Therefore clinoptilolite seems more applicable for municipal waste water with its lower ammonium concentration (Vokacova et al.,

1986), than for anaerobic digester effluent. In experiments with high ion concentrations Farkas et al. (2005) determined the ion selectivity of clinoptilolite. Α high selectivity was observed, with the order of preference being $Mg^{2+} < Na^{+} < Ca^{2+} < NH_{4}^{+} < K^{+}.$ Different to polymeric resins, clinoptilolite has a higher selectivity for monovalent ions. Wang et al. (2007) found a similar order. The order of monovalent ions of these experiments, $H^+ < Na^+ < NH_4^+ < K^+$, is in accordance with their findings.

Eq. 1. Ammonia/Ammonium balance

$$[NH_{3}] = \frac{[NH_{3} + NH_{4}^{+}]}{1 + \frac{[H^{+}]}{K_{a}}} = \frac{[NH_{3} + NH_{4}^{+}]}{1 + 10^{pK_{a} - pH}}$$
$$pK_{a} = 4x10^{-8}xT^{3} + 9x10^{-5}xT^{2 - 0.0356}xT + 10.072$$

0.1 M HCl was used to lower the pH from 8.05 to 5. As a result, a significant increase of the CEC by 27 % was observed. This is in contrast to other experiments where only little effect in the range of pH 5 and 8 (Karadag et al., 2006) is reported. In other studies the optimum pH for ammonium removal is pH 6-7 (Sheng and Chang, 1996;

Factors influencing the ammonium adsorption

Feed with decreased pH. Within the tested ion exchangers, Amberjet 1500 H proved to be the resin with the highest CEC. Further experiments were conducted with this resin to test the impact of a pH decrease in the feed solution. Ammonia-ammonium equilibrium in solution is largely pH dependant (Hedström, 2001) and it stands to reason that only the ionised from can be removed from solution by ion exchange (Thornton et al., 2007). At the current conditions of pH 8.05, 95.7 % is present as ammonium according to Equation 1.

Chen et al., 2002). Below pH 5 a significant reduction of the CEC is expected due to the higher hydrogen ion concentration, which causes competition for sites, resulting in a reduction of the performance. A higher pH in the effluent is due to protons replacing already adsorbed sodium, which also causes the high Na⁺ concentration in the effluent.



Figure 4. Experiments (a) with substrate at pH 5 and (b) enhanced flow rate (both Amberjet 1500 H)

Contact time. Another experiment addressed the evaluation of the contact time for ion exchange (Figure 4b). While contact times in batch experiments range up to 5 d to reach equilibrium (Weatherley and Miladinovic, 2004), the empty bed contact times (EBCTs) in dynamic column experiments are in the range from 1.5 to 15 min. After a standard EBCT of 12 min in the experiments described above, the flow rate of 1.26 cm/min was tripled to 3.77 cm/min (= 15 BV/h) resulting in an EBCT of 4 min. This enhanced flow rate had no significant impact on the CEC, only the elution of all different cations occurred at nearly the same time distinct sequence of the single no breakthrough curves could be observed. Also the slope of the ion breakthrough was less steep, indicating that towards the end of the capacity the reduced contact time was insufficient for full adsorption. These results coincide with the reports of other authors (Semmens et al., 1977), who claim that the shapes of the breakthrough curves depend on the flow rate. In major scale experiments even flow rates of 40 BV/h were successfully applied to treat effluent of a fertilizer factory (Leakovic et al., 2000). However, this was only possible because of the lower NH₄-N concentration of 176 mg/l but also underlines the high cation-exchange capability and quick reaction rate of polymeric resins (Farkas et al., 2005).

Exhaustion of the adsorption capacity. After 10 circles under standard conditions the CEC did not show a significant decrease. Ji et al. (2006) observe a 0.2 % decrease of CEC after 5 cycles, but most experiments are done over a longer period. Ancuta et al. state 99.8 % - 97.0 % CEC after 100 cycles, also Lahav and Green (1998) observe a constant CEC.



Figure 5. (a) Experiments after 10 circles and (b) with reduced amount of regeneration (both Amberjet 1500 H)

Regeneration of resins and long term stability. Both upflow and downflow applications were tested in other lab scale experiments for regeneration (Hedström, 2001). The downflow mode seems more practical and therefore was used in these tests. For scientific purposes, e.g. to evaluate the sorption capacity, often a 10fold stoichiometric ratio of cations is applied to ensure complete regeneration. In opposition to that, in practical applications, the amount of regeneration chemicals is kept as low as possible, since regeneration can make up to 80 % of the process costs (Lahav and Green, 1998; Dimova et al., 1999). In general, the higher the concentration of the ions in the eluate and the smaller the volume of the eluate, the higher the regeneration efficiency of the regenerant. The usage of a highly concentrated regenerant in combination with a long EBCT can help to keep the amount of washing brine as small as possible. Still certain limits have to be obeyed. A certain flow rate is required to transport the ions out of the column, otherwise an equilibrium forms between the washing solution and the resin. Furthermore, highly concentrated acids for regeneration can damage the resin beads. E.g. Leakovic et al. (2000) used highly concentrated nitric acid of (56 wt. %) regeneration, for but this is not recommended by the resin producers. The effect of concentrated hydrochloric acid is much milder since it has no oxidative properties.

In the investigated case, the regeneration with 5 BV of 2 M HCl (10 meq/ml) at a flow rate of 1.26 cm/min achieved a full regeneration. This amount of regeneration brine is equivalent to a 5fold stoichiometric ratio. Ancuta et al. (2005) use only 0.7 BV of a 20 % HNO₃ (2.45 meg/ml) at a flow rate of 0.13 cm/min for the resin Amberlite 252. The back draw of this small employment of chemicals is the lower degree of regeneration between 36.9 % and 47.6 %.

Some studies consider this the normal operation range: in practical applications it is difficult to obtain an operating exchange capacity that exceeds 50 % of CEC (Nguyen, 1997). According to information provided by the producers of the resins 60 % recovery is recommended as the typical operation range. The order of the elution of cations was similar to the order of the breakthrough after adsorption, ammonium being eluted first, followed by sodium and potassium with their stronger affinities. The elution of ammonium has the concentration peak from 1.5 to 2.5 BV washing solution, at 5 BV all ammonium is eluted, while it takes almost 10 BV, before all the potassium is eluted. To minimize acid requirement, a regeneration was performed with 3 BV. In the following experiment exhibited a slightly reduced CEC of 2.12 meq/ml (91.7 %) (Figure 5). This shows, that 3 BV are sufficient to elute ammonium and also most of the potassium and sodium cations. For cost considerations. the 3 regeneration with BV is more recommendable. In such a case an enhanced regeneration is necessary after a couple of circles to remove Mg²⁺ and Ca²⁺. Even if they present only are at minor concentrations, they have a much higher sorption affinity than the monovalent ions (Chen et al., 2002). Also other literature data suggests, that calcium ions are strongly sorbed to the exchanger and permanently ion exchange decrease its capacity (Vokacova et al., 1986; Hedström, 2001) and therefore need to be removed from time to time.

Recommendations for a practical application

The results of the laboratory scale experiments served as the basis for the design of a full scale plant at the given site. A downflow mode is recommended as it requires less pumping effort. To keep costs for regeneration low, a regeneration level of 60 % was chosen. For the treatment of 2 m^3/h RO permeate, an ion exchanger volume of 850 1 is needed, to perform regeneration every 12 h. Instead of hydrochloric acid the use of sulfuric acid is suggested, which is not only less costly but even provides two protons per molecule. Approx. 100 1 of sulfuric acid (50 % w/w) are calculated for regeneration. The high concentration will help to keep the amount of washing brine small. In certain applications calcium sulfate precipitations caused problems but that is not expected at the low calcium concentrations herein.

Practical tests have demonstrated that the residual washing brine can be recycled to the reverse osmosis. Sulfate, as a big anion, is retained by the RO membrane, and therefore also an equal amount of cations will be removed (Hochstrasser, 2007). The RO concentrate will be enriched with nitrogen and sulfur, which makes it more precious as fertilizer. As final usage, the RO concentrate can be dewatered into a dry fertilizer. Surplus heat is available from the combined heat and power station of the biogas plant. Alternatively, the RO concentrate can also be used as liquid fertilizer. Since it is very concentrated, less transport costs arise.

Even though the preceding RO removes all particles, still precipitates can form and lead to cloggings or hydraulic short cuts which can significantly decrease the efficiency of the column. During the experiments, cloggings were also caused by gas bubbles. They can occur when the low pH in the ion exchange column releases CO_2 or adsorbed NH_4^+ turns to gaseous NH_3 , when the pH rises after the CEC is exhausted. In any case, to remove cloggings, facilities for back flushing should be provided.

CONCLUSIONS

Ion exchange proved to be a successful and stable process step to upgrade the anaerobic digestate treatment and the achieved results provided valuable data for the design of a full scale plant. The legal limits for disposal into public water bodies could be met by both the polymeric strongly acidic resins and clinoptilolite, while the nutrients were recovered in the washing brine. Due to higher exchange capacities, reactivities and long durabilities, the polymeric resins are more recommendable than clinoptilolite. Ammonium removals of more than 99 % at contact times of 12 min were achieved. For a more economical application, the flow rate can even be increased. The regeneration with acid containing a 3 fold stoichiometric ratio of protons is sufficient to maintain the cation exchange capacity.

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MGP groundwater treatment: Evaluation of physical and biological treatment methods including a polishing pond

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Abstract

At a former manufactured gas plant in Vienna, Austria, a remediation project is under progress. The planned measurements include the excavation of the core contaminated area and two lines of extraction wells and an infiltration gallery. These wells work as a hydraulic barrier to protect the surrounding groundwater. The extracted water is to be treated in an on-site purification system. Pilot trials were performed in order to optimize the proposed groundwater treatment process. Within a 9 month research programme different physical and biological process steps were evaluated. The treatment focused on the typical pollutants found at former gas work sites in particular, hydrocarbons, PAHs, BTEX, phenols, cyanides and ammonia.

The investigated process comprised an aerated sedimentation, a submerged fixed film reactor (SFFR), a multi-media filter and an activated carbon filter. A hydraulic retention time (HRT) of 7 h or 3.5 h was maintained over the whole treatment process. The setup proved to be highly efficient. While with regard to overall COD reduction all treatment steps contributed more or less equally, the degradation of the target contaminants PAHs and BTEX occurred mainly in the bio-filtration reactor. The total reduction of these contaminants was more than 99.8 %. A very satisfactory effluent quality was achieved. All water quality parameters were below the Austrian legal requirements for direct discharge into open water bodies. However, it was also demonstrated that appropriate pre-treatment was essential to overcome problems with clogging due to precipitation of tar and sulfur compounds.

Additionally UV-Radiation was tested as a disinfection tool and as means to prevent biological clogging of infiltration wells. It was found that bacteria were reduced by 3-5 log steps. On the other hand, UV radiation made inert organics bio-available and hence might stimulate microbial regermination.

In further investigations the purified water was fed to a polishing pond with a residence time of 48h. The pond was planted with reed, water hyacinths and duck weed. While this pond did not contribute much to a further degradation of contaminants it proved to be useful in a "biological" monitoring. Within short time an impressive diversity of aquatic life established. Further eco-toxicological tests and even the exposure to fish (koi and grass carp) introduced into the pond proved the high water quality. Beside the achievement of eco-toxicological and chemical limits, public acceptance is very important for remediation projects. A polishing pond with a vital flora and fauna can largely contribute to make the efficiency of the decontamination process visible to the public.

Keywords: Groundwater remediation, MGP, Pilot-scale, Pump-and-treat, Polishing Pond, UV-Irradiation

1. Introduction

1.1 Site description

At the former MGP site in Simmering (Vienna/Austria) 8.6 billion m³ town gas were produced between 1900 and 1960. At the same

time the typical by products (tar, gas scrubber waste) occurred at an estimated amount of 500,000 t which were disposed right on the site. During WW II the tar disposal and other facilities were destroyed by air strikes resulting in heavy contamination of the soil and groundwater. Located in an aquifer only 300 m distant from a river, this MGP site with a size of 325,000 m² was classified as subject to remediation acc. to Austrian law ALSAG [1] in 1996. In 2000 it was categorized class 1, giving it the highest priority.

To evaluate the site, groundwater samples of 187 bores at different places and depths were analyzed. The groundwater stream was found to be complex, since the general flow direction (south-east) was interfered by an underground tube close by. The chosen remediation concept includes the excavation of the core contaminated site and the establishment of a hydraulic barrier to protect the surrounding aquifer. The extracted groundwater will be treated on-site. For the later implementation of the hydraulic containment 21 extraction wells and 3 monitoring wells were drilled downstream of the site. Two of these bores were used for the pilot plant experiments.

1.2 Scope of the investigations

The objective of the pilot study was to assess options for a full scale long-term plant, in order to be cost-effective while meeting all environmental obligations. Recommendations are to be made, on which treatment steps have to be implemented in a pump-and-treat system. Most of the treated groundwater will be recycled up-stream of the contaminated site through an infiltration gallery. Nevertheless, part of it has to be discharged to ensure hydraulic containment. Hence, the principal aims of the study were: i) to acquire data about the performance of the physical and biological treatment steps, ii) to evaluate, if problems occur during operation of the treatment plant, and how to overcome them. For discharge of the treated groundwater three different options were considered with increasingly stringent legal standards:

- 1. discharge into sewerage system
- 2. discharge into the adjacent river
- 3. re-infiltration into the aquifer

2. Material and methods

2.1 Groundwater

Two of the mentioned bores exhibiting the highest contamination levels were selected for the 9 month pilot plant experiments, one located near the former tar disposal ("well 1"), the other one at the former naphthalene scrubber ("well 2"). An overview over the quality of the groundwater is provided in Table le 1. The groundwater had a constant temperature between 13.1 and 13.7 °C and a constant pH between 6.7 and 7.4 throughout the year.

Parameter	ΡΑΗ [μg/l]	Naphtalene [µg/l]	Benzo(a) pyren [µg/l]	Benzene [µg/l]	BTEX [µg/l]	Phenols [mg/l]	Cyanide [mg/l]
Well 1	789 - 865 ^a	608	<0,03	366 - 512	742 - 806	0,04 - 0,08 ^b	0,18 - 0,25 ^c
Well 2	216 - 745 ^a	66	<0,03	247 - 547	271 - 635	0,21 - 0,53 ^b	0,0 - 0,18 ^c

Table 1: Groundwater quality in well 1 and well 2

Parameter	TOC [mg/l]	COD [mg/l]	HC [mg/l]	NH₄ ⁺ [mg/l]	NO ₂ ⁻ [mg/l]	Fe ²⁺ [mg/l]	Mn ²⁺ [mg/l]	S ²⁻ [mg/l]
Well 1	6,0-6,4	24 - 37	2,4 - 3,0	3,1 – 3,9	<0,01	2,7 – 3,2	0,35 – 0,46	3,12 – 3,48
Well 2	4,32 - 13,0	21 - 61	0,21 – 1,1	3,2 – 7,1	<0,01	0,24 - 0,48	0,12 – 0,21	9,9 - 17,6

^a sum of EPA 16

^b phenol analytics provided by Geoscience Center Goettingen, Germany

^c easily purgeable cyanides

The groundwater of both wells came in with comparable COD concentrations in a range of 21 – 68 mg/l. However, several parameters differed significantly. Well 1 had higher concentrations in hydrocarbons, phenols, and sulphur, while well 2 had higher concentrations in PAHs and BTEX.

2.2 Pilot plant design

The pilot plant comprised physical and biological treatment steps. These were: an aerated sedimentation, a submerged fixed film reactor (SFFR), a multi-media filter (MMF) and activated carbon filters (GAC). The general layout and principle processes of the pilot plant are presented in Figure 1.



Figure 1: Scheme of the pilot plant setup,

SED	Sedimentation/Flotation
BioH, BioK	Submerged fixed film reactors (SFFR)
GAC I, GAC II	Granulated activated carbon filters
MMF	Multi-media filter
P1, P2	Pumps
S1, S2	Storage tanks for back flusk

The principal design data are presented in Table 2:

Process ste	эр	Volume	HRT high/low	Comments		
SED		18.1 m³	5h/2.5h	Aeration rate: 1.5 - 4.0 Nm ³ /h		
SEED	BioH	1.87 m³	1.04h/0.52h	Packing material: expanded clay, pellets d = 6 - 8		
SFFK	BioK 1.58 m ³ 0.		0.88h/0.44h	mm; aeration rate = $1.5 \text{ m}^3/\text{h}$		
MMF		2.3 m ³	0.63h/0.32h	Filling: hydro anthracite, fine sand, coarse sand,		
GAC I or G	AC II	1.5 m³	0.42h/0.21h	AC pellets "Donaucarbon CC50P "		
Polishing pond		10 m³	48h	Surface area = 16,6 m ² , treatment of a partial flow		
UV Irradiat	on	-	0.4h/0.13h	treatment of a partial flow		

Table 2: Process steps of the pilot plant

2.3 Data collection, sampling, and analysis

The pilot plant was controlled by a programmable logic controller. Data about flow, pressure, temperature and pH were recorded automatically every hour. Samples were taken periodically from the influent and effluent. Additional samples were taken after each process steps to determine performance of the single components. Complete analyses of all essential parameters such as COD, PAHs, hydrocarbons, phenols, BTEX, cyanide and ammonia were done according to standard methods.

Other specific analytical methods included: Determination of assimilable organic carbon (AOC) according to the method described by van der Kooij (1982) [2], determination of the inhibition of the mobility of *Daphnia magna Straus* [3] – ISO 6341; acute toxicity test of water samples on the light emission of Vibrio fischeri (ISO 11348 Part 1-3, luminescent bacteria test) [4].

2.4 Schedule of Experiments

Experiments were conducted for 9 months, treating either 1 l/s or 2 l/s with hydraulic retention

times (HRT) all over the treatment steps of 7 h and 3.5 h, respectively. The experimental stages were as shown in Table 3.

Table 3: Experimental stages of the pilot treatment plant

St	age (Q = I/s)	Period, well
0	Start-up	40 d, well 1
1	Standard hydraulic loading rate (flow rate 1 l/s), phosphate dosage	65 d, well 1
2	Standard hydraulic loading rate (flow rate 1 l/s) without phosphate dosage	30 d, well 1
3	High performance (flow rate 2 l/s)	55 d, well 1 + 2
4	Introduction of UV, Bio-GAC and polishing pond (1 l/s)	90 d, well 1

3. Results and Discussion

Operational experience and general performance of the plant

After the inoculation sufficient time was provided for the establishment of an appropriate biological activity in the SFFRs. Within the first 40 days effluent quality reached a stable level and the pressure in the SFFRs increased slightly, indicating biofilm growth. This date was considered as the end of the start-up and the beginning of the test phase.

The removal rates of the two different sized SFFRs were marginally different, with BioH offering a higher HRT showing a subtly better performance. SFFRs were not flushed back but a back flush of the MMF was done every 2 weeks in stage 1, 2 and 4, in the high performance stage every 3 - 6 days. The back flush conditions were 2 min air up flow (40 m³/h) and 5 min water up flow (32 m³/h). Since the detected phosphoruslevels were below the optimum ratio of COD:N:P (200:5:1) a certain test phase was devoted to the possibly positive effect of phosphorous addition. However, the addition of phosphate showed no clear evidence of improved biological removal of contaminants, even while the COD:N:P ratio might suggest phosphorous limitation.

Appropriate pre-treatment turned out to be a critical issue to achieve good results and to maintain stable operation conditions as the groundwater turned out to be a difficult matrix. At contact with air in the first process step the turbidity increased largely and the groundwater became greyish-white. The main reason was the formation of sulphur but beside that also iron and lime precipitates as well as tar-like components were observed. A thick greyish floating layer on

the sedimentation tank occurred. An elementary analysis of the flotate (HEKAtech, CHNSO Analyser) verified the high content of sulphur, 43.6 % - 74.7 % of dry mass, while the carbon content was only 5.4 - 9.8 %. The precipitates caused several problems such as constrictions in pipes, clogging of pumps and disturbed measurement devices, like flow meters and pH and oxygen sensors.

Probably due to the elevated particle concentration after the MMF the pressure drop in the final GAC I increased relatively quickly and it had to be substituted by the second GAC II for stage 3 and 4.

Removal of contaminants

The tested pilot plant configuration proved to be a highly efficient system for the removal of the target contaminants. During stages 1 and 2 at a flow rate of 1 I/s high effluent quality could be achieved, meeting the Austrian legal requirements for disposal into public water bodies which was a main treatment goal. At double flow rate the effluent quality worsened but was still reasonably good.

COD

COD is an overall parameter for organics. All process steps contributed to the removal of COD (**Fehler! Verweisquelle konnte nicht gefunden werden.**). The decrease in the sedimentation is obviously due to removed sediments and floating particles. The SFFRs fulfilled their expectations quite well. However, the data also show that a significant percentage of the COD is not eliminated. A residual concentration between 9 - 15 mg/l was neither biodegraded nor absorbed on the activated carbon. Additional analyses of the

BOD₅ proved; that the readily biodegradable organics were removed between 95 % and 99 %.

HC-Index

The SFFRs achieve significant removal of contaminants. Even during the high performance stage the residual HC concentration is below 0.1 mg/l. This reconfirms the good bioavailability of the hydrocarbons. The following MMF does not contribute much, but the GAC absorbs the residual HC below detection limit (0.03 mg/l).

EPA-PAHs

The analysis for aromatic compounds focused on the EPA-16-PAHs, representative for a class of carcinogenic and mutanogenic substances. The influent could be treated successfully in the SFFRs with removal rates between 77 % and 98 %. Residual concentrations of PAHs were almost completely adsorbed in the subsequent activated carbon treatment. After the GAC the removal rate was in all stages beyond 99.5 % with total levels in the range from 0.27 µg/l to 0.88 µg/l.

<u>BTEX</u>

BTEX are highly volatile toxicants. Therefore most of the BTEX were removed in the aerated sedimentation/flotation unit. Exhaust air analyses verified that BTEX are almost completely stripped and no biological degradation was observed.

Phenols 1 4 1

The sum concentration of phenolic compounds of both well 1 and well 2 were around $300 - 500 \mu g/l$. Phenols were only partly consumed in the SFFRs and were mostly adsorbed to the activated carbon. Final levels in the GAC effluent were 5 - 10 $\mu g/l$.

Cyanides

The concentration of total cyanides found in the influent was 0.5 - 0.7 mg/l. Total cyanides proved to be inert and no significant degradation was observed in the process steps. The reason is that cyanide compounds found at former MGP sites mainly occur as relatively nontoxic iron-complexed forms, such as ferric ferrocyanide, rather than the highly toxic free cyanide forms. The Austrian legal requirements for disposal into water bodies have no regulation for total cyanides, but easily purgeable (=free) cyanides are limited with less than 0.1 mg/l. This requirement could be achieved with effluent concentrations mostly under detection limit (0.01 mg/l).

The contribution of the different processes to the removal of organic compounds is provided in **Fehler! Verweisquelle konnte nicht gefunden werden.**2. An overview over the achieved effluent quality is provided in Table 4Table 4.



Figure 2. C-Removal (TOC) of all process steps of the pilot plant

3.3 Performance of the polishing pond

A polishing pond was installed for further treatment of the effluent. The pond was planted with reed (*Phragmites australis*), water hyacinths (*Eichhornia*), water lettuce (*Pistia Stratiotes*) and

duck weed (*Lemna*). Together with the plants also several smaller animals such as snails and insects were introduced. Within a short period a versatile fauna evolved. A wide variety of zoobenthos was observed, proving a very good water quality according to the index of biological integrity. Nutrients in the groundwater (NH_4 -N > 4 mg/l) lead to a slightly enhanced algae growth, which was then controlled by an increased snail population.

However, as it can be taken from Table 4, the pond did not contribute much to a further degradation of residual concentrations of the contaminants. On the other hand, the impressive diversity of aquatic life proved to be useful as an instrument for "biological" monitoring" High water transparency and no observable odour emissions completed the picture. In this context, the potential ecotoxicity of the effluent was investigated. In Figure 3 it can be seen that the influent exhibited a very severe inhibitory effect. After treatment, the luminescence of *Vibrio fischeri*, being the most widely used ecotoxicity test, showed a significant reduction of the inhibition, with results comparable to the adjacent river, while the acute toxicity, tested with *daphnia magna* (Figure 4), also showed a largely reduced inhibition, but still at a considerable level.

A potential reason for the performance of the polishing pond beyond initial expectations is the relatively low hydraulic retention time of 24 hours. In this case, the retention time was chosen according to expected groundwater flow to be treated and the available area at the site which would not allow the establishment of a larger pond. Beside the achievement of the given treatment

goals, public acceptance is very important for remediation projects. A polishing pond with a vital flora and fauna, and even the exposure to fish (grass carp, koi), as also done in this investigations, can largely contribute to make the efficiency of the decontamination process visible to the public.

Table	4:	Austrian	legal	limits	for	water	disposal	and	effluent	comparison	before	and	after	treatment v	with
		polishing	pond	(av. v	alue	es over	a90 d p	eriod)						

Parameter	Reinfiltration into aquifer	Discharge into public water bodies	Discharge into sewerage system	Effluent before polishing pond	Effluent after polishing pond
PAH	0.1 μg/l (Austrian 6- PAH)	100 µg/l (ЕРА-16-РАН)	-	0.27 µg/l (EPA-16-PAH)	0.20 µg/l (EPA-16- PAH)
Benzene	0.1 µg/l	-	-	< 0.1 µg/l	< 0.1 µg/l
BTEX	Benzen & Toluene: max 0.1 µg/l-each	100 µg/l	100 µg/l	< 0.1 µg/l	< 0.1 µg/l
Phenols	-	0.1 mg/l	20 mg/l	< 0.01 mg/l ^a	< 0.01 mg/l ^a
Cyanide (easy purgeable)	0.03 mg/l (Total Cyanides)	0.1 mg/l	0.5 mg/l	0.66 mg/l	0.48 mg/l
TOC	-	25 mg/l	-	5.48 mg/l	5.50 mg/l
COD	-	75 mg/L	-	12.94 mg/l	13.68 mg/l
HC-Index	0.06 mg/l	10 mg/l	20 mg/l	< 0.1 mg/l	<0.1 mg/l
NH ₄ -N	0.03 mg/l	10 mg/l	-	5.50 mg/l	4.36 mg/l
Fe	-	2.0 mg/l	-	0.27 mg/l	0.29 mg/l
Mn	-	-	-	0.16 mg/l	0.15 mg/l
SO4 ²⁻	-	-	400 mg/l	137 mg/l	131 mg/l



Figure 3. Results of Lumistox-test of the in- and effluent and after post treatment in a polishing pond. For reasons of comparison also the data for the adjacent river are provided



Figure 4. Results of Inhibition test of the mobility of *Daphnia magna* in- and effluent and after post treatment in a polishing pond. For reasons of comparison also the data for the adjacent river are provided

Effect of UV irradiation

Since biological treatment was employed, an elevated bacterial count was suspected in the effluent. Responsible authorities recommended a final disinfection step, in particular when re-infiltration is considered. Therefore a UV irradiation device was installed after the GAC. The reduction of total bacterial count at 22°C and 37°C and of indicator bacteria was investigated at

various dosages rates. From Figure 5 a) and b) it can be seen that the UV irradiation is very effective to eradicate bacterial micro-organisms, whereupon indicator bacteria were already at an inconspicuous level in the influent (Figure). On the other hand, it is also known that UV irradiation has no long term effect and re-growth of micro-organisms may occur. The analysis for assimilable organic carbon is a parameter to measure bio-available organic matter. AOC refers to a fraction of the total organic carbon, which can be utilized by bacteria, resulting in an increase in biomass concentration. The results showed (Figure 66 a) that with intensification of the UV dose the available organics increase, probably due to the formation of bacterial cell debris or the break down of non degradable organic components which were still present in the effluent. Only at very high dosage rates the assimilable organic carbon lowered again as a results of complete oxidation of part of the organic matter to CO_2 . These finding was confirmed by additional investigation addressing the regermination potential (Figure 66 b). With regard to that, UV irradiation can be seen as an efficient tool for disinfection, but on the other hand, regrowth will rapidly lead to even increased bacterial counts.



Figure 5 a, b: Total bacterial count (a) and bacterial count of indicator organisms (b) in the effluent after the application of increasing UV irradiation rates



Figure 6 a, b: Assimilable organic carbon (a) and re-germination potential (b) in the effluent after the application of increasing UV irradiation rates

4. Conclusions and Recommendations

9 months of pilot plant experiments proved the efficiency of the employed pump-and-treat system, the Austrian legal requirements for disposal into public water bodies were achieved. Appropriate pre-treatment turned out to be a critical issue to achieve good results and to maintain stable operation conditions. Attention should be paid, that this first treatment step is a sturdy construction which can be easily maintained and it should allow simple removal of float- or settleable precipitates.

The chosen system turned out to be highly reliable and the SFFRs contributed much to the degradation of the typical MGP contaminants. Expanded clay pellets as a packaging material was highly adequate, as confirmed by stable degradation rates throughout the whole operation period. The addition of phosphate showed no clear evidence of improved biological removal of contaminants, even while the COD:N:P ratio might suggest so. The final GAC fully assured the effluent quality and the residual concentrations of the target contaminants were close to detection levels.

The polishing pond, which was operated for 3 month, did not significantly improve the effluent quality, probably due to the relatively low retention time of 48 h. On the other hand a high diversity of plants and animals made achievement of a good groundwater remediation visible. Ecotoxicity tests proved this success.

Further investigations with UV irradiation to decrease the bacterial count in the effluent demonstrated high efficiency. But after this initial effect on the long term enhanced bacterial growth is triggered, due to the release of a higher amount of bio-available carbon. This might even stimulate biological clogging of infiltration wells when effluent is re-injected.

In summary the investigated pump-and-treat system proved to be an efficient and cost effective means of hydraulic containment and groundwater protection and the gained data provide a sound data basis for the design of the future full scale treatment to be installed.

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Micro filtration and Ultra filtration in the Treatment of Anaerobic Digester Effluent

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Annotation

The effluent of an anaerobic digester is highly concentrated in organics and nutrients. A setup of solid separation, submerged micro filtration and reverse osmosis is employed for treatment, showing weaknesses of the micro filtration concerning permeability and clogging. Ultra filtration pipe modules made of polysulfon and polyvinylidene fluoride of 20, 80, 100 and 250 kDa pore size are tested herein. The smaller pore size and the higher cross flow velocity ($v \ge 4$ m/s) prohibit clogging and achieve a better effluent quality and a much more stable operation than the micro filtration.

Keywords

Micro filtration; ultra filtration; anaerobic digestion; size exclusion

INTRODUCTION

Biogas has become an increasingly important source of alternative energy in Austria. While 119 biogas plants were operated by the end of 2003 the number almost doubled to 231 by the end of 2005 [Energie-Control]. Not only the number, but also the size of the plants increased, leading to massive amounts of digester effluent, being still rich in organics but also in nutrients. The disposal of this effluent has become the bottle neck of this sustainable energy source. А setup consisting of solid separation, micro filtration and reverse osmosis (RO) should achieve nutrient recovery and a RO permeate quality which should meet disposal quality into public water bodies. It turned out, that the flow of the micro filtration decreased immediately and also heavy aeration could not prevent clogging. Analysis of the solids proved, that a major part of the total suspended solids were particles smaller than 45 µm. Experiments with ultra filtration pipe modules were expected to overcome the problems of the submerged micro filtration modules for two reasons: i) the UF pore size is smaller

than the particle diameter. The removal of biological particles and colloids by membranes depends closely on their pore size [Saddoud et al], while it is not clear yet, if the suspended solids, the colloids or the solutes of sludge contribute most to membrane fouling [Wisniewski et al, Defrance et al, Bouhabila et al] ii) higher cross flow velocity prevents fouling. Experiments range from 1.2 m/s [Bae et al] to 5.0 m/s [Saddoud et al].

The aim of this study was to test different organic and inorganic membrane materials with different pore sizes. Operational parameters like crossflow velocity and pressure should be evaluated. 4 ultra filtration tube modules with organic membranes and a micro filtration tube module with an inorganic membrane were applied. These results were compared to submerged the hollow fiber micro filtration, which is currently in charge. Beside flux, permeability and pressure the experiments also evaluated the permeate quality (TS, COD, TP, TN).

MATERIAL and METHODS

Substrate

A 500 kW biogas plant in Austria is operated in co-digestion with cow manure (50 %), kitchen and bio waste (25 %),

slaughter waste (15%), and energy crops (10%). The effluent is pre-treated with a screw press (mesh size = 1 mm) and a vibration sieve (mesh size = 0.25 mm) for solid separation.

Table 1: Parameters of the pre-treated Anaerobic Digester Effluent (total solids, total nitrogen, ammonium nitrogen, chemical oxygen demand, total phosphorus and pH)

TS [%]	TN [mg/l]	NH ₄ -N [mg/l]	COD [mg/l]	TP [mg/l]	рН
4.09	9,433	7,290	44,700	1,198	8.24

Analyses of all essential parameters were done according to standard methods for the examination of water and waste water [APHA, AWWA and WEF]. Temperature and pH were measured with a multiparameter instrument (340i, WTW). The TS (4.09 %) consists mainly of total suspended solids (TSS = 2.89 %), a minor part are total dissolved solids (TDS = 1.20 %). A sieve analysis revealed, that more than 50 % of the TSS are particles with a d $< 45 \mu m$. Anaerobic digester effluent is considered a demanding substrate for filtration [Novak et al], due to its particle size distribution around 10 μm [Elmaleh et al]. Since living microorganisms are included, the fouling process is complex [Bae et al].

Table 2	. Applied	membranes
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				Pore	Transmem-	Sur-	Cross-
Producer	Tradename	wembrane	Material	size	brane pressure	face	flow
		туре		[kDa]	[bar]	[m²]	[m/s]
Mitsubishi	SUN 10534 LP	MF	PSU ¹ (sub- merged)	500	-0.20.5	630	0.002 ²
PALL	8507040	MF	Ceramic ³	400	0.2 – 4.2	0.176	4.0
MEMOS	M-C40-12-VFU250	UF	PVDF ⁴	250	0.4 - 6.0	0.396	4.0
MEMOS	M-C40-08-SU100	UF	PSU	100	0.4 - 6.0	0.377	4.0
MEMOS	M-C40-08-VFU80	UF	PVDF	80	0.4 - 6.0	0.377	4.0
MEMOS	M-C40-08-SU20	UF	PSU	20	0.4 - 6.0	0.377	4.0

¹ Polysulfon

² submerged hollow fiber module, no crossflow, but constant airflushing ($Q = 450 \text{ m}^3/\text{h}$)

 3 Al₂O₃

⁴ Polyvinylidene fluoride



Figure 7: Experimental set up

The filtration tests were performed at 20 \pm 2 °C at transmembrane pressures from 0.2 to 6.0 bar, which exceeds the common range of other UF experiments between 1.25 and 2.25 bar [Elmaleh et al, Saddoud et al]. For the experimental set up a multistage centrifugal pump (CRN 2, Grundfos) was employed. It was continuously variable from $0.0 - 2.0 \text{ m}^3/\text{h}$. The influent and permeate flow were measured with a digital flow meter (Promag, Endres & Hauser) and a rotary flow meter (SK 50, Georg Fischer). Pressure was measured with mechanical manometers (Type 111.10, WIKA) and a digital manometer (DPI 705, DP Control).

For chemical cleaning NaOCl (Neuber) was used as basic detergent. Furthermore an acidic cleaner based on HNO₃ (P3

Ultrasil 75, igefa) was used. Both reagents were applied for 1 h in 0.2 % dilutions (v/v). The cleaning order was basic-water-acidic-water and achieved sufficient flux regeneration.

RESULTS and DISCUSSION

The pretreatment of the anaerobic digester included a solid separation, consisting of a screw press (d = 1mm) and a swing sieve (d = 0.25 mm). Still the content of total solids was high (TS = 4.09 %). Further analysis revealed, that more than 50 % of these solids had a particle size < 45 μ m. These particles caused clogging at the submerged hollow fiber membrane. Therefore the operation conditions of the submerged MF were unstable with several breakdowns (Figure 2).



Figure 2: Flux of the submerged hollow fiber micro filtration during 1 month

Modules with smaller pore sizes were employed to overcome the clogging. The crossflow velocity of 4 m/s. as recommended by the manufacturer, was necessary. In UF experiments of Bae et al the crossflow velocity is controlled at 1.2 m/s, but our experiments at 3 m/s showed significantly worse results than at 4 m/s, meaning, that a cake layer formed, that considerably contributed to the total resistance. The membrane with the smallest pore size of 20 kDa achieved the highest flux and permeability, the 80 kDa membrane came in second, followed by 100 kDa and 250 kDa. This suggests, that size exclusion separates colloidal solids,

only the smaller particles clog the pores (Figure). The flux rates of the SU 20 module between 18.3 l/m².h and 23.6 l/m².h are better than in similar experiments [Fuchs et al, Bae et al, Saddoud et al 03/2007, Zhang et al]. The flux of the submerged MF is significantly lower than those achieved by tube modules, although a comparison can not be made, since these are different systems. The submerged hollow fiber module applies suction (0.2 - 0.5 bar), while the tube modules apply pressure (0.2 - 6.0)bar).



Figure 3: Flux comparison of various crossflow tube modules

All tube modules showed a stable process. The permeability proved to be best at operational pressures between 2.0 and 2.5 bar (Figure). These results are better in comparison to the submerged hollow fiber module with an average permeability of 6.457 l/h.m².bar over one week. While the smaller pores proved to be more efficient, there was no significant difference among the organic materials. Polysulfon and PVDF showed similar performances. The ceramic module could not compete with

the organic membranes., but is considered the most durable membrane [Kim et al]. It is assumed, that the poorer performance of the inorganic membrane is due to the higher tendency for scaling [Kang et al]. The very high content of ammonium in this substrate, with the presence of phosphate and magnesia are likely to form struvite precipitations, which is considered a major problem in membrane treatment for anaerobic digester effluent [Kang et al, Choo et al].



Figure 4: Permeability comparison of various crossflow tube modules



Figure 5: Comparison of the submerged MF module and the inside-out UF module

The results of the most efficient crossflow tube module (pore size = 20 kDa) were compared with the submerged hollow fiber module, implemented in the original treatment process. The UF tube module showed a significantly higher flux and a higher permeability, also the effluent was better in all parameters (**Figure**, **Figure**). Furthermore a pore size \leq 100 kDa retains all microorganisms [Saddoud et al, 03/2007].

A considerable reduction of contaminants in the SU 20 module was observed. The

COD concentration decreased to 3,665 mg/l and the TP concentration was reduced to 38.84 mg/l (removals of 91.8 % and 90.5 % respectively). The total suspended solids were removed completely. Still the ammonium concentration of 6,284 mg/l was very high (13.8 % removal). For the elimination of this small cation further treatment is necessary. Reverse osmosis or ion exchange could achieve sufficient nutrient recovery and disposal quality of the effluent.



Figure 6: Effluent quality of the UF tube module and the submerged MF module

CONCLUSION

Anaerobic digester effluent is a difficult for purification. substrate High contaminant concentrations demand a stable process with efficient cleaning treatment. Crossflow tube membranes proved to fulfil these requirements much better than a submerged hollow fiber module. The membrane with a pore size of 20 kDa proved to be more efficient than pore sizes of 80 kDa, 100 kDa and 250 kDa. A flux of 18.3 l/m²h at 2.0 bar transmembrane pressure was achieved, the

crossflow velocity was kept at 4 m/s. The contaminant removal showed satisfactory results in COD and TP removal, while ammonium could not be reduced much. Therefore further treatment is necessary for full nutrient recovery in order to fulfil legal requirements for disposal into public water bodies and prohibit eutrophication. Despite higher pump energy consumption and smaller membrane area, UF tube modules are recommended, since they provide a stable process and a good effluent quality.

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Pilot plant results for groundwater treatment at the former gas work remediation site "Leopoldau" in Vienna, Austria

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Abstract

At the contaminated site of a former manufactured gas plant in Vienna, Austria a remediation project is underway since 2003. The planned measures include encapsulation of the contamination core area by a cut off wall of a total length of 1300 m and the establishment of a hydraulic barrier employing a pump and treat system. Water drawn from both the core area and the extraction wells will be treated in an on site purification process. On account of the long duration of the extraction and in order to optimize the groundwater treatment process it was decided that pilot trials are to be performed. The finally selected plant configuration comprised flotation, biological activated carbon filtration and activated carbon filtration. It was demonstrated that the investigated pilot plant turned is a highly efficient system for the removal of the target contaminants. Flotation turned out to be a simple and reliable pretreatment process. The pre-requisite for successful process operation of the subsequent biological activated carbon filter was a proper nutrient supply and sufficient oxygen availability. At such conditions, it was possible the achieve drinking water level with regard to the Austrian regulation, for the target components PAHs, BTEX and mineral oil. In the investigated case these components were relatively easily biodegradable and rapid biological breakdown occurred. The obtained results provide a sound basis for the design and dimensioning of the future full scale groundwater remediation process.

Keywords: contaminated site, gas plant, biological activated carbon filter, flotation, PAHs, BTEX

Introduction

The manufactured gas plant "Leopoldau", Vienna, Austria, was built in 1899, covering an area of about 420.000 m². At this location over a period of 70 years about 10 billion m³ manufactured gas from coal was produced until 1966 when the gas production was closed down. During the second world war the site was repeatedly bombed. As a result, both groundwater and soil are contaminated by site specific pollutants. Main contaminants are: PAHs, BTEX, hydrocarbons and inorganics (sulfides, ammonia and cyanides).

A project to remediate the site is underway since 2003. The planned measures includes the following activities:

- i) encapsulation of the contamination core area by a cut off wall of a total length of 1300 m,
- ii) installation of a series of 15 extraction wells downstream in groundwater flow direction as a hydraulic barrier to intercept groundwater flow and reinijection of the purified water upstream of the contaminated site.

Within the screen walls, the groundwater table is regulated by means of continuos withdrawal of approximately 18 m³/h. The amount drawn from the maximum extraction wells is 130 m³/h of which a 110 m³/h will be recirculated after purification. To ensure hydraulic interception, a difference of 20 m³/h together with the surplus derived from the core area will be discharged either to the public sewerage or, alternatively, re-injected downstram of the site system. The later is only possible if an sufficient grade of purification is achieved, where the concentration of the target components meet the criteria of the Austrian drinking water regulation.

On account of the long duration of the extraction and the required high standard for process performance, the company "Wienenergie Gasnetz GmbH", the current owner of the site, has decided that pilot trials are to be performed.

The pilot plant was established in late 2004 and comprises coagulation/flocculation, sedimentation or flotation, and activated carbon filtration. The feed water originated from two wells located inside the core area.

Composition of contaminated groundwater

Table 1 provides an overview over the contaminants present in the groundwater.

parameter	groundwater Leopoldau	TWV	Wr. Kanal-VO
sum of PAHs	0.1 μg/L ^a (70 - 1539 16-EPA ^b)	0.1 µg/L ^a	-
benzapyrene	<0.01 µg/L	0.01 µg/L	-
benzene	1 - 19 μg/L	1 μg/L	-
BTEX	4.7 - 157.8 μg/L	-	
phenoles	< 0.05 mg/L	-	20 mg/L
cyanide	0.06 - 0.11 mg/L	0.05 mg/L	0.5 mg/L
TOC	2.5 - 8.4 mg/L	-	
permanganate oxidizability	3.8 - 5.3 mg/L O ₂	5 mg/L O ₂	
mineral oils	1.7 - 3.2 mg/L	-	20 mg/L
$\mathrm{NH_4}^+$	0.08 - 0.47 mg/L	0.5 mg/L	
NO ₂ ⁻	0.6 - 2.9 mg/L	0.1 mg/L	
Fe	0.14 - 4.1 mg/L	0.2 mg/L	
Mn	0.31 - 0.52 mg/L	0.05 mg/L	

Table 1: Composition of the contaminated groundwater and relevant target concentrations in accordance to the Austrian drinking water regulation (TWV) and the Viennese regulation for discharge in the public sewerage system (Wr. Kanal-VO)

^a in the Austrian TWV only the PAHs benzo-(b)-flouranthene, benzo-(k)-flouranthene, benzi-(ghi)-perylene, inden-(1,2,3-cd)-pyrene are listed

^b Sum of 16 PAHs according to EPA regulations

Pilot plant set up



Figure 1: Schematic drawing of the pilot plant facility

The choice of treatment methods in the plant was based on an intensive survey of available literature and full scale experience in which several treatment options were considered. Finally, the pilot plant comprised the following treatment processes:

- Coagulation/flocculation: flow through reactor with 3 mixing chambers 1.5 m³ each
- Sedimentation or flotation: volume of sedimentation zone 10.5 m³, surface area 5.2 m²
- Biological activated carbon filter: filter height 1.7 m, filter volume 1.8 m³
- 2 activated carbon filters: filter height 1.5 m, filter volume 0.9 m³, each

A schematic drawing of the pilot plant facility is presented in Figure 1.

Operational conditions

Two different hydraulic residence times were applied. In setting one the water flow was 7.2 m³/h resulting in residence time of 15 min. in the biological activated carbon filter and 7.5 min. each in the two subsequent activated carbon filters. The total residence time in the pilot plant including pretreatment was 2.3 hours. In setting two the water flow was reduced to 3.6 m³/h and hence, the residence times were doubled.

For start up, the biological activated filter was inoculated with 10 l activated sludge (suspended solids 9 g/L) which derived from a industrial waste water treatment plant treating effluents from an oil refinery. The sludge was mixed with about 3 m³ feed which was than pumped through the filter. After a period of approximately one month, when still almost no biological activity could be observed, an additional supply of nutrients was implemented. Nitrate and phosphate were added in such amounts to obtain at a COD:N:P ratio of 100:5:2 in the influent.

Performance of the pretreatment process

The process of coagulation/flocculation with ferric chloride and flocculant aid was primarily performed on a laboratory scale. Good flocculation and contaminant removal was observed. At a concentration of 0.1 Mol/m³ Fe³⁺ as a coagulant with the support of 0.1 g/m3 flocculant aid, removal rates of 60 - 70 % were obtained for turbidity and mineral oils. As well 45 % of the PAHs were removed. However, it was not possible to repeat this promising results in practice, due to the a suboptimal system design and also due to fluctuation in influent composition. Therefore coagulation/flocculation was not further followed.

As a substitute a floatation step was installed. By this simple pretreatment process approximately 20 % of the incoming COD and 40 - 80 % of the main target contaminants, mineral oil, BTEX and PAHs were removed. Moreover, the floatation served a double purpose as it provided the oxygen for the microflora in the biological activated carbon filter. A small amount of pollutants were stripped into the off-gas, where about about 20 ppm C were measured, with BTEX and naphthalene as the main components.



Figure 2: Concentration profile of PAHs in dependence of the filter bed depth at different specific throughputs. left: situation before and after implementation of the nutrient supply, right: situation during a period of oxygen deficiency and after re-establishment of appropriate oxygen supply

Performance of the activated carbon filters

During the first month, the performance of carbon filter the activated was unsatisfactory due to an insufficient biological activity. While the effluent quality was reasonably good, a more detailed analyses of the concentration profiles of the target contaminants within filter bed revealed impending the breakthrough. The plain adsorbance capacity of the chosen granulated activated carbon material turned out to be relatively low. Breakthrough of PAHs and BTEX was predicted to occur already at a specific throughput of $6 - 7 \text{ m}^3$ groundwater per kg activated carbon.

As а main reason for the poor biodegradation, a phosphate deficiency in the groundwater was identified. After implementation of the nutrient supply, biological activity developed rapidly and fast degradation of the contaminants within the filter bed was observed (Figure 2, left side). The important contribution of biological breakdown of the contaminants is also underlined by the chart at the right side of Figure 2. For a period of $1^{1}/_{2}$ weeks a failure of the aeration device in the flotation occurred, which caused an oxygen limitation in the biological activated carbon filter. Again very fast accumulation of contaminants occurred.

At this conditions all target components were already removed in the upper part of the biologically activated carbon filter. The subsequent activated carbon filters, established only for safeguard purposes, had almost no impact on effluent quality. After re-establishment of appropriate oxygen supply, the concentrations of PAHs, BTEX and mineral oil dropped immediately to very low concentrations. The corresponding oxygen consumption in the filter was in the range of 6 - 7 mg/L.

In second test period the hydraulic residence time was doubled. This lead to a further improvement of effluent quality, in particular with regard to removal of NH_4^+ and NO_2^- as well as iron and manganese.

noromotor	low HRT	high HRT	
parameter	water flow: 7.2 m ³ /h	water flow: 3.6 m ³ /h	
	0.1 µg/L	$< 0.1 \ \mu g/L$	
Sulli OI PAHS	(<1.1 µg/L)	(<1.1 µg/L)	
benzapyrene	<0.01 µg/L	$< 0.01 \ \mu g/L$	
benzene	$< 0.9 \ \mu g/L$	<0.9 µg/L	
BTEX	$< 3.6 \mu g/L$	<3.6 µg/L	
phenols	< 0.05 mg/L	< 0.05 mg/L	
cyanide	n.d.	0.06 - 0.11 mg/L	
TOC	2 mg/L	1.85 mg/L	
permanganate oxidizability	3 mg/L O ₂	3 mg/l O ₂	
mineral oil	<0.1 mg/L	<0.1 mg/L	
$\mathrm{NH_4}^*$	0.2 mg/L	0.1 mg/L	
NO ₂ ⁻	0.2 - 0.7 mg/L	< 0.05 mg/L	
Fe	0.10 mg/L	0.05 mg/L	
Mn	0.49 mg/L	0.19 mg/L	

Table 2: Effluent quality obtained with the pilot plant at the two different hydraulic residence times

Conclusions

The tested pilot plant configuration proved to be a highly efficient system for the removal of the target contaminants. Flotation turned out to be a simple and reliable pre-treatment process. The prerequisite for successful process operation of the subsequent biological activated carbon filter was a proper nutrient supply and sufficient oxygen availability. At such conditions, it was possible the achieve drinking water level, with regard to the Austrian regulation, for the target components PAHs, BTEX and mineral oil. In the investigated case these components were relatively easily biodegradable and rapid biological breakdown occurred. The obtained results provide a sound basis for the design and dimensioning of the future full groundwater remediation scale process.

Comparing centralised and decentralised anaerobic digestion of stillage from a large-scale bioethanol plant to animal feed production

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ABSTRACT

A comparison of stillage treatment options for large-scale bioethanol plants was based on the data of an existing plant producing approximately 200,000 t/yr of bioethanol and 1,400,000 t/yr of stillage. Animal feed production – the state-of-the-art technology at the plant- was compared to anaerobic digestion. The latter was simulated in two different scenarios: digestion in small-scale biogas plants in the surrounding area versus digestion in a large-scale biogas plant at the bioethanol production site. Emphasis was placed on a holistic simulation balancing chemical parameters and calculating logistic algorithms to compare the efficiency of the stillage treatment solutions. For central anaerobic digestion different digestate handling solutions were considered because of the large amount of digestale. For land application a minimum of 36,000 ha of available agricultural area would be needed and 600,000 m³ of storage volume. Secondly membrane purification of the digestate was investigated consisting of decanter, microfiltration, and reverse osmosis. As a third option aerobic wastewater treatment of the digestate was discussed. The final outcome was an economic evaluation of the three mentioned stillage treatment options, as a guide to stillage management for operators of large-scale bioethanol plants.

Key words | anaerobic digestion, animal feed, bioethanol, digestate treatment, stillage

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INTRODUCTION

The production of ethanol is one of the major fermentation processes worldwide and is set to increase in the future owing to a surge in demand for biofuels. A contributing factor of this demand is due to political forces. The EU intends to raise renewable energy to 5.75% in the fuel sector. The Austrian government aims to raise this even to 10% by 2010. The construction of large-scale bioethanol plants will increase, therefore stillage management and stillage treatment processes will have to be explored in greater detail.

This study evaluates the stillage treatment process currently in use at an existing bioethanol plant (200,000 t/yr of bioethanol) which mainly uses com and doi: 10.2166/wst.2008.515 wheat as substrates. The standard procedure is processing stillage to dried distiller's grains and solubles (DDGS) which is used as animal feed. However, DDGS production consumes a lot of energy owing to the evaporation and drying processes. For that approximately the same amount of energy is consumed as in the entire bioethanol production process (Friedl *et al.* 2005), on top of the fact that the bioethanol production is already very energyconsuming because of the distillation process. Due to rising energy prices bioethanol plant operators will have to optimise energy consumption, to avoid a negative impact on the costs of ethanol production (Wilkie *et al.* 2000; Pfeffer *et al.* 2007). Therefore, this study investigates

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scenarios for energy co-production by simulating anaerobic digestion (AD) from the stillage produced at the bioethanol plant. Energy is produced which can replace fossil fuels at the plant. In addition, by using biogas as energy source green house gases can be reduced decisively and a better eco-balance can be achieved. This is very important since the EU is planning a certification scheme for biofuels where a minimum of green house gas reduction will be demanded.

This study focuses on AD as promising option for stillage treatment. Wilkie et al. (2000) have stated in a technical evaluation of various stillage treatment options that AD is economically viable and sustainable. Besides, less sludge is produced by AD than in aerobic treatment of stillage, where also significant aeration power would be required. One advantage of AD could be the possibility to use grains of lower quality for ethanol production: rye or grains contaminated with mycotoxins cannot be processed to animal feed, so if these substrates had no negative effect on ethanol production they could be used and their residues converted to biogas. If AD is concerned the efficiency of the process no longer depends on the market for DDGS but on the energy market, where the prices are expected to keep increasing. There are two main scenarios to realise AD of the produced stillage: either to build a central biogas plant at the bioethanol production site or to sell the stillage to surrounding small-scale biogas plants. Thus these two different strategies were investigated in the study comparing them to the state-of-the-art DDGS production.

METHODS

Through a modular design of the simulation process an easy comparisons was made possible (Figure 1). The model of the theoretical processes consisted of DDGS production, peripheral AD in surrounding small-scale biogas plants, or



Figure 1 | Satup of the different modules in the simulation model.

central AD. For the latter, three digestate treatment options were simulated: membrane purification, aerobic wastewater treatment, and land application as fertilizer.

Each module containing process flows was treated in a black box-approach with input and output parameters, or divided into sub-modules which were treated alike. The process flows in the model were calculated as mass and energy balances using the measured parameters. For the calculation of anaerobic digestion also data from the working group's data base were integrated into the simulation. From data provided by industry every module and sub-module could be given a financial value, so that a coherent overall picture of the simulated process options was obtained and the comparison could be made. For machinery a 10 year amortisation period was considered. Operating costs and energy costs were calculated but no costs of manpower entered into the comparison.

Characterisation of process flows

Samples were taken from the bioethanol plant to characterize the different process flows. The following parameters were obtained using *Standard Methods* (APHA 1998): Total Solids (TS), Volatile Solids (VS), and Chemical Oxygen Demand (COD). Also the nitrogen content in the process flows was considered in the simulation by Total Kjeldahl Nitrogen (TKN). The biochemical methane potential (BMP) of the stillage was evaluated through anaerobic batch fermentation tests according to the modified norm DEV S6, DIN 38 414-S6 (DEV 2005) at 35°C using as inoculum fermented sludge from a biogas plant fed by pig manure, corn whole crop silage and grass silage.

DDGS production

In the DDGS production process the stillage is separated into a solid phase (wet cake) and a liquid phase (centrifugate). The centrifugate is concentrated to syrup by vacuum evaporation. This syrup is then mixed again with the produced wet cake and dried to DDGS. For the comparison the investment costs of the machinery and the costs for carbon dioxide certificates were included. For energy costs the heat energy needed was calculated in fossil gas consumption. However, the vacuum concentration step (from about 10% TS to about 30% TS) was not considered as extra costs since internal energy from ethanol condensation is used in the process. In addition, to demonstrate the influence of rising energy prices three different scenarios were calculated: present energy costs, a 50% rise in energy costs and a 100% rise. For the DDGS price two scenarios were calculated. First a price of 200€/t which was about the price assumed in Friedl *et al.* (2005), secondly, a lower price of 100 €/t. The reason for this was that bioethanol production is increasing worldwide and with an increase of DDGS on the market the price could be lower.

Central AD

Because of the large quantities of stillage (1,400,000 t/yr) an innovative scheme for high throughput was presented and calculated in this study. Therefore a pre-treatment step with microbiological hydrolysis was considered where part of the solid substances is liquefied. The remaining solids are separated by a decanter and converted to compost. For composting additional costs of 40 €/t were calculated. The liquid hydrolysed phase is fed into high throughput digesters. The produced biogas is converted to energy by combined heat and power units. For the calculation of the revenue the actual energy prices paid by the bioethanol plant were considered. For the digestate treatment three different scenarios were calculated, as described here.

Fertilizer application

In this module the surrounding agricultural areas at the production site were considered with an application limit for nitrogen of 210 kg N/ha (according to national regulations). Since digestate cannot be applied all year over a storage capacity of half a year had to be considered, calculating a 10 year amortisation period for storage containers. Digestate transportation and application was calculated assuming 20 m³ application carts. The benefit of digestate fertilizing was calculated from nitrogen (N), phosphorus (P) and potassium (K) content of the digestate.

Membrane purification

Here the setup and the costs were calculated according to the membrane treatment process presented in Klink et al. (2007). This module therefore consists of a decanting step, and consecutive purification by ultrafiltration followed by three steps of reverse osmosis.

Aerobic wastewater treatment

Lacking experimental data of an existing biogas plant joined with an aerobic wastewater treatment plant, this module was estimated from the expenses of a standard large-scale aerobic wastewater treatment plant with an amortisation period of 15 years. In addition, the costs of an additional carbon source were calculated since it is needed to achieve entire denitrification. The reason for this is that most of the organic matter is metabolised in AD, whereas a high nitrogen concentration remains in the digestate. Because bioethanol is present at the plant in great quantities, it was taken as external carbon source in the simulation. In addition, it poses a good carbon source and it is easy to calculate its costs. Nevertheless in practise alternative cheap carbon sources have to be identified and used. About 3-5kg CSB of carbon are needed for the denitrification of 1kg nitrate (Gerardi 2002). According to these values two different scenarios of the addition of ethanol were calculated: First the addition of ethanol-CSB to TKN in the relation 1:1, second in the relation 2:1. The ethanol price was taken as 640€/m3.

Peripheral AD

In this module the stillage is digested in small-scale (500 kW_{al}) biogas plants in the surroundings. Every biogas plant was calculated as its own profit centre, to guarantee a realistic stillage price that the biogas plant operators are able to pay. In order to raise the stillage price, transportation costs and logistics were considered to be the responsibility of the bioethanol plant operator. This option was evaluated by determining revenue of stillage sale and costs of stillage transportation.

RESULTS AND DISCUSSION

The methane potential and the characteristics of the corn and wheat stillage produced at the plant are presented in Table 1. The nitrogen (TKN) level in wheat stillage was Table 1 Characteristics of corn and wheat stillage

	pitt	COD (g/kg)	TS [%]	VS [%]	THIS LIPTING	BMP (m ³ /tVS
Com stillage	4.7	159	9.7	9.1	45	611
Wheat stillage	5.5	147	10.2	9.3	6.9	579

quite high with 6.9g/kg which could have a negative effect on process stability when carrying out continuous fermentation. For a more realistic approach to estimate the methane production in the continuous process only 75% of the measured maximum methane potential was assumed in the following comparison.

DDGS production

At the bioethanol plant about 4,022 t/d of stillage are produced and processed to about 415t/d of DDGS (mounting to over 145,000 t/yr). The calculated process flows are presented in Figure 2 which were used for calculating the mass and energy balance.

The results of the economic evaluation of the DDGS production are given in Table 2. For the scenario where a DDGS price of 200 ϵ /t is assumed the margin is 22.4 million ϵ (Mil. ϵ)/yr and for the second (100 ϵ /t DDGS) 7.9 Mil. ϵ /yr. This demonstrates the great influence of the DDGS price on the evaluation. Especially in the 100 ϵ /t DDGS scenario you see the great difference concerning rising energy costs: Considering present energy costs the margin is 7.9 Mil. ϵ /yr, if energy costs rise 100% the margin drops to less than a half (3.0 Mil. ϵ /yr).



Figure 2 Process flows in DDGS production.

Central AD

The large-scale biogas plant would mount to about 21 MW_{al} and 25 MW_{therm}. In Figure 3 the simulated process flows are shown, using membrane technology as digestate treatment. The expenses for AD (without calculating digestate treatment) are 7.2 Mil ϵ /yr, about one third (2.3 Mil. ϵ /yr) are the costs for composting the not hydrolysed solids. If this fraction could also be used as fertilizer, the expenses for AD would be quite lower. The total revenue for electricity and heat is 19.8 Mil. ϵ /yr.

Digestate treatment

In Table 3 the expenses for the digestate treatment scenarios are presented. For land application as fertilizer 1,200,000 t/yr of digestate have to be applied on a minimum of 36,000 ha of agricultural area and 600,000 m³ of storage volume is needed. Storage costs are 3.1 Mil. €/yr and transportation and application costs are 6.4 Mil. €/yr, total expenses are 9.5 Mil. €/yr. The fertilizer value due to the N, P and K content would mount to 5.5 Mil. €/yr, leaving total expenses of 4.1 Mil. €/yr. Since it is not credible that agriculture would pay the same price for digestate as for fertilizer concentrate, realistic expenses would lie somewhere between 4.1 and 9.5 Mil. €/yr. In addition the local nutrient demand or surplus has to be considered.

The expenses of membrane purification $(5.1 \notin /t \text{ diges$ tate; Klink*et al.* $2007) mounts to <math>6.3 \text{ Mil} \notin /yr$. In the simulation the RO-concentrate (739 t/d, see Figure 3) was assumed as fertilizer without cost or profit, although it has quite a high salt-concentration, so the fertilizing qualities could be questionable.

In aerobic wastewater treatment the expenses turn out to be 5.9 Mil.€/yr (calculating the relation of ethanol COD to TKN to be 1:1) or 9.4 Mil.€/yr (considering a relation of 2:1).

Table 2 Expenses, revenue and margin for DDDS production in dependence on DDDS-price and energy costs

	DD-DS price of 100 6/t			DDGS price of 2004/t		
	Expenses	Revenue Mil. c/yr	Margin Mil.c/yr	Expenses Mil. c/yr	Revenue MIL Cyr	Margin Mil. c/yr
	MIL c/yr					
Today's energy prices	6.6	14.5	7.9	6.6	29.0	22.4
50%-rise	9.0	14.5	5.5	9.0	29.0	20.0
100%-rise	11.5	14.5	3.0	11.5	29.0	17.5

Evaluation of central AD and digestate treatment

For the final comparison membrane purification (with expenses of 6.3 Mil €/yr) was selected as standard process for central AD. This means a margin of 6.2 Mil. €/yr for central AD. Membrane purification is preferable to fertilizer application on the one hand because more than 950,000t of water per year are recycled into the process by membrane purification, on the other hand yearly expenses for land application vary a lot depending on the realistic fertilizer value of the digestate. Finally, fertilizer application of 1,200,000 t/yr is a great logistic challenge, the logistics of membrane purification are more easy to handle for a bioethanol plant operator. Membrane purification of digestate is also preferable to aerobic treatment, because the rather high cost of an external carbon source can be avoided. The carbon (organic matter) of stillage is removed to a great part by AD, so it makes little sense to add again expensive C-source to achieve a stable aerobic treatment. The cheaper one of the two aerobic treatment scenarios



Figure 3 | Process flows of simulated central AD with membrane purification of digentate.

produces expenses of 5.9 Mil €/yr which is comparable to the costs of membrane purification (6.3 Mil €/yr). Since the latter is considered to be more stable and costs are about the same or lower than in aerobic treatment, membrane purification was finally chosen as standard digestate treatment process for the model. Also combinations of aerobic treatment and membrane purification could be a viable solution.

Peripheral AD

This scenario means that the produced stillage would be transported to about 38 smaller-sized nearby biogas plants (with 500 kW_{sl} and $\eta_{el} = 0.35$), at a presumed average distance of 40 km. In the province of Lower Austria where the bioethanol production site is located there exist 100 biogas plants with an installed total capacity of 33.95 MW_{el} (E-Control GmbH 2007). So at least 56% of the energy produced by AD in this province would be provided by the stillage of the bioethanol plant. A realistic price of 1.2 e/t stillage was assumed which results in a revenue of 1.6 Mil e/yr for the operator. To achieve this price transportation costs (of about 8.1 Mil. e/yr) would have to be covered by the bioethanol plant operator. Thus the total expenses of

Table 3 | Expenses of the different scenarios for digestate treatment

	Expenses [ML c/yr]
Fertilizer application (including theoretical fertilizer value)	4.1
Fertilizer application (w/o fertilizer value)	9.5
Membrane purification	6.3
Aerobic wastewater treatment (ethanol-COD:TKN = 1:1)	5.9
Aerobic wastewater treatment (ethanol-COD:TKN = 2:1)	9.4

peripheral AD are 6.5 Mil. €/yr. Since the other two stillage treatment options produce earnings instead of costs, peripheral AD should be disregarded as an option for large-scale bioethanol plants. In small-scale or middle-size bioethanol plants this option can still be a good choice, since by peripheral AD no digestate management is needed which is one of the key issues in central AD and quite cost intensive.

Outcome of the comparsion

The results of the comparison (Table 4) show that under the described conditions (today's energy prices) it is favourable for operators of large-scale bioethanol plants to produce DDGS. However, this is only the case when DDGS can be sold above 100 €/t. If the DDGS price is significantly below this level AD becomes competitive. At a DDGS price of 100 C/t the yearly margin will be about 7.9 Mil. C/yr for DDGS production, whereas central AD will earn 6.3 Mil. 6/yr. Additionally, if energy prices rise by 50% DDGS production will only produce 4.5 Mil. €/yr. So the tendency of DDGS prices and energy prices should influence a plant operator's decision to introduce AD. Rising energy prices always favours AD, since the energy consuming distillation process can be fed with the energy produced and no expensive external energy has to be purchased. If energy prices rise 100% the margin for DDGS production becomes decisively lower than for AD: At a DDGS price of 100€/t the margin will be 3.0 Mil.€/yr and at 200 €/t it will be 17.5 Mil €/yr. Since AD produces energy its margin is higher than both DDGS production scenarios:

Table 4 | Comparison of expanses, revenue and margin for bbits production, central Ab (with membrane purification) and peripheral Ab (including rise of energy prices)

	Margin (Mil. c/yr)
Today's energy prices	
DDGS production (100 €/t DDGS)	7.9
DDGS production (200 €/t DDGS)	22.4
Central AD	6.2
Peripheral AD	-6.5
100% rise in energy prices	
DDGS production (100 €/t DDGS)	3.0
DDGS production (200 €/t DDGS)	17.5
Central AD	25.1

The earnings will be 25.1 Mil.€/yr. This shows that even at a higher DDGS price AD stays the preferable option when energy prices rise decisively.

This study also reveals that at large-scale bioethanol plants central AD is preferable to peripheral AD. The latter produces a minus of 6.5 Mil.€/yr, considering that only a price of 1.2€/t (stillage) can be paid by small-scale biogas plants to assure their positive balances and that the bioethanol plant operator must cover the transportation costs. Central AD, however, earns 6.2 Mil.€/yr at today's energy prices.

CONCLUSIONS

At today's energy prices DDGS production is preferable to AD. Only if the DDGS-price drops below 100 €/t AD becomes competitive. If energy prices rise decisively biogas production will be both an economically and ecologically better option than animal feed production, even if DDGS prices are 200€/t. The main problem for central AD at a largescale bio ethan ol plant is the digestate treatment. As this study shows over 50% of the costs for AD will be due to digestate treatment. Here the treatment by separation processes containing membrane purification seems to be one of the preferable solutions. It is a stable process and the costs are comparable or cheaper than fertilizer application or aerobic wastewater treatment. The results show clearly that the AD in surrounding small-scale biogas plants is no economically viable solution. So if AD is concerned central AD at the plant location is the option to chose. Therefore further research should focus on digestate management. Still data from largescale anaerobic digesters with implemented membrane purification are lacking. So before membrane technology becomes standard technology at biogas plants, however, additional research on this topic should be carried out.

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Air stripping of ammonia from anaerobic digestate

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ABSTRACT

Effluents of anaerobic digestion plants generally show high content of nitrogen compounds. In many cases removal of ammonia is necessary to improve nutrient management e.g. in areas with high animal farming density. Air stripping is a promising technology not only to remove but also to recover the stripped ammonia as a valuable product. In this study the influence of typical pre-treatment technologies and the variation of the process parameters temperature and pH on stripping efficiency were investigated. The alkalinity of the substrate, i.e. the HCO₃⁻ concentration, was identified to be of critical importance. On the one hand it acts as a buffer system which makes elevation of the pH more difficult on the other hand the parallel desorption of CO_2 during NH₃ stripping stabilizes the pH. It was demonstrated that precipitation with lime milk (Ca(OH)₂) for removal of suspended solids and carbonates results in a strong decrease of alkalinity. Hence the pH in the course of the stripping process drops strongly which leads to a lower process efficiency. Therefore lime milk has to be overdosed which leads to an excessive chemical demand. As alternative suspended solids removal by means of microfiltration is proposed. In this case, only a moderate pH adjustment with caustic soda to pH 10 is suggested. To compensate, a high temperature, $80^{\circ}C$, should be applied during to the stripping process. Under such conditions elimination rates of 90% and even higher were achieved.

Introduction

Biogas technology has found great acceptance for power and heat production over the last years, not only because it is considered as a CO₂ neutral energy source but also as an appropriate technology for the treatment of organic waste. Nowadays, operators of biogas plants find themselves confronted with the challenge to find an appropriate technology that guarantees a low cost and long term assured possibility to treat the remaining digestate. In general, the remaining digestate is brought out to agricultural fields and used as a fertilizer. Nowadays biogas plants are often built in a larger scale – due to higher efficiency in the energy production – which leads to an increased use of supra-regional substrates. Hence, the required areas for bringing out the digestate are often not available in the vicinity of the production location. In such a case the legal limitation for bringing out nitrogen compounds requires transportation over long distances.

For that reason treatments for nitrogen removal and recovery have become processes of concern for improving waste management in areas with a nitrogen surplus. Air stripping in combination with absorption (typically sulphuric acid) is a promising technology to remove and recover ammonia from the liquid fraction of the anaerobic digestate (Bonmatí and Flotats (2003), Rulkens *et al.* (1998)).

Best air stripping efficiency can be achieved when a packed column is used, as it guarantees a huge surface and therefore optimal contact conditions of the gaseous and the liquid phase.

The pre-treatment of the anaerobic digestate effluent before entering the stripping column is a critical step, because it has a direct influence on the stripping efficiency and reliability of operation. The parameters that have to be adjusted are:

- content of suspended solids (SS)
- temperature
- pH

pH and the temperature play the key role, as they influence the dissociation equilibrium of NH_4^+/NH_3 and the distribution between aqueous and the gaseous phase. the Furthermore dissolved solids. mainly inorganic ions like carbonates and phosphates, can cause severe problems in the process and may precipitate especially under conditions of high pН and/or high temperatures in the column or heat exchanger (Görisch and Helm (2006)).

Besides the controlled precipitation of the mentioned substances in settling tanks with lime milk (Ca(OH)₂), also stripping of CO₂ is a method often applied in practice.

Several alternative procedures are in use as a pre-treatment before stripping. All of them include a solid liquid-separation. Figure 1 shows two typical pathways for the pretreatment of the anaerobic digestate. Pathway A includes a precipitation step. Frequently lime milk is added to the anaerobic digestate for precipitation, whereas at the same time the pH is lifted up to values from 10 to about 12 (Ozturk *et al.* (2003)). The disadvantage of precipitation with lime is the production of a huge amount of sludge (Kollbach *et al.* (1996)) which has to be removed in a subsequent settler or flotation. On the other hand lime precipitation removes carbonates which might lead to scaling or clogging of the stripping column.

Another pre-treatment option is shown in pathway B. In this case, the separation of the suspended solids from the liquid fraction is done by a centrifuge and subsequently a filtration step (microfiltration or ultrafiltration) eliminates all the of remaining SS. In many cases, carbonates are then eliminated via CO_2 stripping. Due to the elimination of carbon dioxide the pH Even higher pH values can ascends. afterwards be adjusted by the addition of base, e.g. caustic soda.

The purpose of the investigations described herein was to identify the best preconditioning method and the respective process parameters for a digestate from a local biogas plant.



Figure 1: Schema for treatment options of anaerobic digestate
MATERIALS and METHODS

Anaerobic digestion plant

The material used for all experiments was taken from an anaerobic digestion plant in Styria/Austria. The biogas plant uses cow manure, kitchen garbage and other organic waste as substrate. Concentration of NH_4 -N was from 3,970 to 7,842 mg/l (Table 1). The anaerobic digestion effluent taken from the final storage and after microfiltration was stored at 4°C before usage for experiments.

Table 1.	Characteristics	of	anaerobic	digestion	effluent
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Parameter	Unit	Final storage	After microfiltration
TS	%	4.81	1.40
pН		8.20	8.51
CSB	mg/L	51,493.5	10,264.5
TN	mg/L	9,183.5	8,209.8
NH4-N	mg/L	6,732.5	6,522.3
PO4-P	mg/L	1,008.2	428.0

Pre-treatment of the anaerobic digestate

Precipitation with lime milk

Different dosages of lime milk (10%) were added to 500 mL anaerobic digestate effluent in 1000 mL beakers. The samples were stirred for 30 min before the resulting mixtures were then allowed to precipitate for 2 hours. Afterwards alkalinity and pH values were measured.

Elimination of CO₂ with sulphuric acid and pH adjustment

In order to investigate the influence of the presence/absence of carbonates, sulphuric acid with a concentration of 98 % was added to the effluent after microfiltration until a final pH of 4.3. The liquid was stirred for 30 min before the pH was increased with caustic soda to the desired pH. For the pH lifting caustic soda with a concentration of 50 % was added. After the addition of caustic soda the mixture was stirred until the pH got stable.

Stripping of carbon dioxide in bubble reactors

For stripping of carbon dioxide in batch scale, three two litre bottles were used, whereas the first two bottles were for air moistening and the third one contained the sample (Figure 2). In order to obtain the required temperature the incoming air was first mixed with steam. The temperature was controlled in the waterbath and in the inlet of the last bottle (with the anaerobic digestate effluent after microfiltration). A sample was taken every 15 min for a duration of 120 min, afterwards the pH, alkalinity and NH₄-N were determined.

Stripping of ammonia

Stripping of ammonia in bubble reactors

The experimental setup was the same as described in Stripping of carbon dioxide in bubble reactors. A sample was taken every 15 min, afterwards the pH, alkalinity and NH₄-N were determined.



Figure 2: Experimental setup for stripping in bubble reactors

Air stripping of ammonia with a stripping column

The schematic layout of the stripping device is presented in Figure 3. The column has a total height of 1.5 m whereas the filling bodies occupy 1.1 m. The used filling bodies are HIFLOW rings, with a specific surface of 313 m²/m³. The internal diameter of the inner column is 80 mm, the outer column serves as a mantle to guarantee the temperature conditions as adjusted for the experiments. Dimensioning of the column was done with the program RAPSODY (Version 2.18) from the company Rauschert Verfahrenstechnik. Air for stripping was mixed with steam before entering the column to enable saturation of the inflowing air with water and in the same way adjustment of the required temperature. Temperature was measured at all points of entrance and outlet to ensure stable conditions during the stripping process.



Figure 3: Stripping column with preheating of the liquid and the air inflow

RESULTS and DISCUSSION

Pretreatment

Precipitation with lime milk

Addition of lime milk is done to remove phosphate and carbonates and as well to increase the pH. Moreover SS are reduced significantly. Lei *et al.* (2007) found optimization on Ca(OH)₂ dosage at 27,5 g/L for an effectively removal of SS, turbidity NH₄-N, COD and PO₄-P. Furthermore, an addition of only 12,5 g/L was necessary to increase the pH to values \geq 12. Addition of excess lime to prevent the pH from dropping was reported by Cheung *et al.* (1995) for landfill leachate. However, consumption of lime milk was in our case much higher, due to the high content of buffering substances. In order to increase the pH up to a value of 10, addition of 60 g/L lime was necessary (Figure 4). At this pH, 88,2 % of the alkalinity was removed, which leaded to a dimished buffer capacity.

Equation 1 shows the connection of the addition of lime and the precipitation of $CaCO_3$.



 $2Ca^{2+} + 2OH^{-} + 2HCO_3 \leftrightarrow 2CaCO_3 + 2H_2O$ (1)

Figure 4: Removal of alkalinity and increase of pH due to precipitation with lime milk

Stripping of carbon dioxide

The presence of carbonates in the anaerobic digestate affects the stripping process, on one hand, in terms of the reliability of operation due to the precipitation of lime, and on the other hand due to a high consumption of base for increasing the pH. Lei *et al.* (2007) and Marttinen *et al.* (2001) described the increase of the pH when carbon dioxide is stripped at ambient temperature and at relatively moderate air flow rate. After one day of aeration with a

flow rate of 2.5 L/Lmin the pH increased from 7.4 to 9.3.

In our case this was suspected inefficient and therefore a higher temperature ($80^{\circ}C$) and also an increased flow rate 5 (L/Lmin) were considered as convenient process conditions. Figure 5 compares CO₂ stripping at 20°C and 80°C and demonstrates the much higher efficiency of elevated temperature. The elimination of alkalinity behaves oppositional to the pH value (Figure 6): the lower alkalinity gets, the higher the pH gets. Both curves come up to an equilibrium.



Figure 5: Increase of pH due to aeration at 20°C and 80°C and an airflow of 5 L/Lmin



Figure 6: pH and alkalinity in dependence of time at an airflow of 5 L/Lmin and 80°C

Adjustment of the pH

To obtain high efficiency of ammonia stripping at room temperature increasing of the pH up to 10,5 - 11,0 is inevitable (Liao *et al.* (1995)). The consumption of base is an

important cost factor. Efforts, to keep the consumption of chemicals as low as possible and nevertheless achieve the required elimination efficiency of ammonia therefore often play a major role.



Figure 7: Consumption of caustic soda (50%) to digestate (untreated and after addition of sulphuric acid)

It is obvious that buffer systems in the digestate, primarily HCO_3^{-7}/CO_3^{-2-} and NH_4^{+7}/NH_3 , lead to a very high consumption of caustic soda resulting in high operation costs. The average pH value of the untreated anaerobic digestate was about 8.5. In order to increase the pH of the untreated digestate up to 10, 16 mL/L have to be added. For adjustment to higher pH values the consumption of NaOH got drastically higher, e.g. 34.6 mL for pH 11 and 40 mL for pH 12.

When the digestate first was CO_2 removed, in the range from pH 8,5 to pH 10 the progression of the curves was almost the same, whereas for pH values > 10 the NaOH consumption was significantly lower (Figure 7).

Stripping of ammonia

Stripping of ammonia in bottles

In order to investigate the influence of the presence of carbon dioxide on stripping efficiency of ammonia, experiments were carried out in bubble reactors. Two kinds of synthetic ammonia solutions (NH₄Cl and NH₄HCO₃) were compared with the

anaerobic digestate effluent, untreated and CO_2 removed.

According to equation 2, NH₃ is in equilibrium with NH_4^+ . When NH_3 is desorbed to the gaseous phase the chemical force is driving the reaction to the right side and the protons generated lower the pH. During the stripping of the CO_2 the contrary effect occurs (equation 3). Therefore the carbonate prevents a pH change during ammonia removal. Figure 8 illustrates this effect. Both for the microfiltrated digestate and the NH₄HCO₃ solution, the pH remained almost stable even at ammonia removal rates of nearly 100%. In contrast, if the carbonate buffer was removed the pH droped dramatically to levels as low as pH 7. The decline of the pH is due to the lacking buffer capacity. It can also be seen in Figure 8 that the pH of the CO₂ removed digestate is slightly more stable than of the synthetic NH₄Cl solution. The difference in behaviour is presumably due to a buffer capacitiy caused by other constitutents than carbonate, e.g. humic substances.

With the ongoing decline of the pH the amount of free NH_3 present in the solution decreases until no further removal occurs.

$$NH_4^+ \leftrightarrow NH_3 + H^+$$
 (2)



Figure 8: pH in dependence of removed ammonia of synthetic wastewater and anaerobic digestate at and 80°C and airflow of 5 L/Lmin

Figure 9 shows the progress of NH₃ removal with time. When the carbonates of the anaerobic digestate were eliminated by addition of sulphuric acid, total elimination of ammonia was not possible. The curve progression showed a similar behaviour as the NH₄Cl solution and stagnated at a remaining concentration of ammonia at 14% of the starting value during the last 30

minutes, whereas the remaining ammonium concentration of the not CO_2 removed anaerobic digestate was only 0,27%.

In comparison, the elimination rate of ammonia from the NH_4HCO_3 solution behaved the same as the not CO_2 removed effluent and showed much higher efficiency (Figure 9).



● Digestate → Digestate, CO2 removed -□- NH4HCO3 -△- NH4Cl

Figure 9: Remaining NH₄-N in dependence of time at 80°C and airflow 5 L/Lmin

The course of alkalinity of the samples stripped at 80°C can be seen in Figure 10. With the ongoing process, alkalinity got more and more exhausted. The difference between the NH₄HCO₃ solution and the digestate is only due to different start concentrations of NH₄-N



→ Digestate, CO2 removed O Digestate

Figure 10: Alkalinity of synthetic wastewater and digestate (with and without CO₂ removal) in dependence of time at 80°C and airflow 5 L/Lmin

Stripping efficiency was as also tested without pH adjustment.

A lower pH value favours the formation of undissolved CO₂ and therefore enhances its desorption. If desorption of CO_2 is higher than for NH₃, the pH is even going up. In Figure 11 it can be seen that the pH is

converging to almost the similar value as the sample with a pH adjusted to 10.

In consequence, the effectiveness of the ammonia removal was in both cases almost the same.

Table 2 shows the air amount required for a certain percental reduction of ammonia.

If 50 % reduction is the goal, than the air demand is 1.34 fold the theoretical value for the pH adjusted digestate whereas it is 1.91 for the untreated one. Still this means that 43.5% more air is required if the pH is not changed. For higher elimination rates e.g. 90%, the multiple of the minimum airflow becomes even higher and increased to a value of 2.9 for the untreated digestate.

Thereby the difference between the untreated digestate and the pH increased sample show no big difference in respect to the multiple of the minimum airflow. This small difference might be caused by the higher pH of the sample treated with caustic soda in comparison to the untreated digestate.

Table 2: Minimum airflow and multiple of minimum airflow for certain elimination rates at 80°C

Elimination rate	of	Minimum airflow	Applied [L/L]	airflow	Multiple airflow	of	minimum
NH4-N [%]		[L/L]	untreated	pH 10	untreated	pH 10	
50		103	197.2	138.1	1.9	1.3	
80		168	413.4	334.6	2.5	2.0	
90		189	551.1	485.9	2.9	2.6	



-□- NH4-N, untreated → NH4-N, pH 10 → pH, untreated → pH, pH 10

Figure 11: Remaining NH_4 -N of digestate (untreated and after pH adjustment up to 10) in dependence of time, at 80°C and airflow of 5 L/Lmin



Figure 12: Remaining alkalinity of digestate (untreated and after pH adjustment up to 10) in dependence of time, at 80°C and airflow of 5 L/Lmin

Air stripping of ammonia with a stripping column

Stripping in a packed column is much more efficient than stripping in a batch reactor due to the higher exchange surface. The actually required air demand in a stripping column is normally 1.2 to 1.5 higher than the theoretical minimum air demand (Perry and Green (1997)) and a more economic process to achieve higher NH₄ removal levels. For the further experiments an elimination rate of at least 80 % was set as the removal goal.

Setting of flow conditions

To find out optimal liquid flow rate to achieve the required elimination rate, experiments with the stripping column were carried out at a pH of 10, a constant airflow of 20 m³/h and temperatures of 60 and 80°C. Figure 13 shows that higher flow rates lead to reduced stripping efficiency. At a temperature of 80°C and a flow rate of 20 l/h only 9.63 % of the starting concentration of NH₄-N remained in the effluent whereas the remaining concentration of NH₄-N at 60°C was 22,5 %. For the following experiments the conditions of 80°C and a liquid flow rate of 20 l/h have been considered as appropriate.



Figure 13: remaining NH_4 -N in the effluent of the stripping column in dependence of various liquid flow rates at 60 and 80°C and airflow of 20 m³/h

A stripping column is mainly characterized by the parameters column height, column diameter, filling material, number of transfer units (NTU) and the height of transfer units (HTU).

Due to constant air and liquid flow in our experiments, column parameters were only maintained at a temperature of 20°C. Under these conditions the theoretical column height and the real column height were almost the same (Table 3, 1.1 m in comparison to 1.19 m).

For higher ammonia removal rates, the necessary number of transfer units increases. In our experiments the NTU value reached its maximum with 2.8 at 80°C. On the other hand, due to higher efficiency, the HTU value decreases and the resulting column height is determined through

H=NTU*HTU_{opt} (with HTU_{opt} at least two times higher than HTU). To investigate the influence of the temperature and the pH value, we maintained the flow conditions constant, with the consequence that the air flow was higher than the determined minimum (5.21 times higher at 80°C). In the praxis the columns are generally built higher in place of higher air flow due to economical considerations. Nevertheless, the effective elimination rate of ammonia obtained matches well with the theoretical calculations. For the obtained elimination rates, the determined deviation with a maximum of 2.5 at 50°C was quite high, but considering the small column diameter and the thereby associated wall effects, the performance was considered as satisfactory.

Table 3: Theoretical column parameters and elimination of ammonia at pH 10

Temp. [°C]	Remaining ammonia [%]	Remaining ammonia [mg/L]	NTU	HTU [m]	Theoretical column hight [m]	Deviation of the theoretical column hight
20	61.89	4,853.6	0.9	0.66	1.2	0.92
50	43.36	3,400.7	1.0	0.22	0.44	2.50
60	28.52	2,237.1	1.5	0.16	0.48	2.29
70	13.93	1,092.9	2.4	0.12	0.58	1.91
80	8.85	694.3	2.8	0.09	0.50	2.18

Influence of temperature

The influence of temperature is a main factor for stripping efficiency. In Table 3 the remaining ammonia concentrations and percentages are listed. With increasing temperature, the rest concentration of ammonia in the effluent can be strongly diminished. Again, for reasons of comparison the presence/absence of HCO₃⁻ was investigated. Similar results as in the bubble reactor were obtained. While the pH of the effluent from the not treated feed did not fall lower than 9.5 at 80°C, the pH of the CO_2 removed sample decreased to a value of 8.5. A temperature increase did not much further contribute to the final removal rate (Figure 14).



Effluent, CO2 removed Effluent -D- pH Effluent, CO2 removed A pH Effluent

Figure 14: Remaining NH₄-N and pH in the effluent after stripping at pH 10 and airflow of 20 m³/h.

Influence of pH

As an air temperature of 80°C can be obtained using the waste heat from the gas engine, and it showed promising elimination results, further experiments were conducted at that temperature. Fig. 15 shows the results when varying the other main factor of influence, the pH.

At pH of 10 the residual concentration is already lower than 10 %. Any further reduction causes a strong raise of the chemical costs which are required for increasing the pH (Fig. 16).



Figure 15: Remaining NH_4 -N, alkalinity and pH in the effluent after stripping at 80°C and airflow of 20 m³/h in dependence of the pH



Figure 16: Removed NH4-N and adjusted pH in dependence of NaOH added at 80°C and airflow of 20 m3/h

CONCLUSION

To guarantee good operation reliability and high stripping efficiency the anaerobic digestate has to be pretreated. Precipitation with lime is advantageous due to the simultaneous suspended solid reduction, removal of carbonates and pH increase. However lime precipitation consumes a high portion of the alkalinity. This alkalinity keeps the pH at a constant level during the stripping process because of the simultaneous stripping of CO_2 . Therefore the removal of alkalinity has to be compensated by the addition of a corresponding amount of base. E.g. an alkalinity of 400 - 500 mMol/L corresponds to 21 mL/L - 26,2 mL/L NaOH (50 %). Therefore lime is usually added in excessive amounts, which leads to high operational costs and problems with later neutralization.

To reduce chemical demand and sludge formation it is more convenient to opt for the second pathway proposed. In such a case the pH should not be raised above a value of 10. In order to still have efficient removal rates it is rather recommended to increase the temperature to 80°C. Under such conditions removal rates of up to 90 % or even above can be obtained.

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COMPARING DIGESTATE TREATMENT OPTIONS FOR THE ANAEROBIC DIGESTION OF STILLAGE AT A LARGE-SCALE BIOETHANOL PLANT

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ABSTRACT: A comparison of three different digestate handling scenarios for a simulated large-scale biogas plant were calculated in this study: These were the application as a fertilizer on the surrounding agricultural areas, aerobic wastewater treatment and membrane separation. The biofuel production was used as field of interest, since digestate handling is very important in anaerobic digestion when treating large amounts of substrate. The process data from a large-scale Austrian bio-ethanol plant (200,000 t/yr) were the basis for this comparison. According to this the anaerobic digestion of the accumulating stillage (1,400,000 t/yr) was simulated. This would produce about 1,200,000 t/yr of digestate. For land application due to nitrogen application limits, a minimum of 360 km² of available agricultural area would be needed and 600,000 m³ of storage volume. For the scenario of membrane purification of the digestate the investigated process consisted of a decanter, ultrafiltration, and three steps of reverse osmosis. As a third option aerobic wastewater treatment of the digestate is investigated, where the addition of additional carbon source is the main problem. The final outcome is an economic evaluation of the three mentioned digestate handling options.

Keywords: biogas, bio-ethanol, anaerobic digestion, centralized biogas production, digestate, stillage, wastewater treatment.

1 INTRODUCTION

The EU intends to raise renewable energy to 10% in the fuel sector by 2020. The Austrian government even aims to raise this to 20%. Consequently the construction of large-scale biofuel plants will increase, where a lot of organic residues will accumulate at the production site. These residues are often used as animal feed stuff [1].

Anaerobic digestion (AD) is here a valuable alternative to increase the amount of renewable energy in biofuel production [1, 2, 3]. Especially since the EU plans to implement a certification system for biofuels where at least 35% reduction of carbon dioxide emission in comparison to fossil fuels should be achieved. All these influences may increase the construction of large-scale biogas plants, however the biggest challenge in these concepts is the problem of treating the digestate, the residue from AD.

This study investigates three possible digestate treatment options for a simulated AD of the stillage (1.4 Mio. t/yr) from an existing large-scale bioethanol plant (200.000 t/yr) in Austria. These digestate treatment options [4] are the following:

• application as fertilizer on surrounding agricultural lands

• purification by membrane technology and liquid-solid separation

• aerobic wastewater treatment.

2 MATERIALS AND METHODS

The comparison is based on the data from the process-flows at the bio-ethanol plant and the calculated nutrient loads of the digestate (1,200,000 t/yr) from a simulated large-scale biogas plant at the plant location [1]. The three digestate treatment options were calculated according to conditions which are presented in the following:

2.1 Application as fertilizer

digestate treatment option the In this surrounding agricultural areas at the bio-ethanol plant were considered. From this area the fields needed for the application of the animal manure which is produced in the region was subtracted. The remaining area was assumed to be available for digestate application. The Austrian regulations were considered as application limit where a maximum of 210 kg (N) ha-1.a-1 can be applied [6]. Since digestate cannot be applied all year over a storage capacity of half a year had to be calculated and a 10 year amortisation period for these storage containers was considered. Digestate transportation and application costs were calculated assuming 20 m³ application carts.

The theoretical benefit of digestate fertilizing (theoretical fertilizer value) was calculated from nitrogen (N), phosphorous (P) and potassium (K) content of the digestate.

2.2 Aerobic wastewater treatment

Lacking experimental data of an existing biogas plant joined with an aerobic wastewater treatment plant, this scenario was estimated from the expenses of a standard large-scale aerobic wastewater treatment plant. An amortisation period of 15 years was considered and the costs were estimated due to COD (Chemical Oxigen Demand)load of the accumulating digestate.

Because of the high nitrogen (N) content an external carbon (C)-source is needed to achieve purification. Since ethanol accumulates at the plant in large quantities and is very good biologically available it was considered as C-source. The costs of the standard wastewater treatment and the costs for the external C-source mounted to the entire

treatment costs. Nevertheless in practice an alternative cheap carbon source should be identified and used. For this treatment option two different scenarios of the addition of ethanol were calculated: first an addition of ethanol-COD to TKN in the relation 1:1, second in the relation 2:1. The ethanol price was also calculated in two scenarios one with $500 \notin m^3$ and the other with $640 \notin m^3$.

2.3 Membrane purification

This scenario consists of a decanting step where the solid phase is separated from the liquid phase of the digestate. Then the liquid phase is purified by ultrafiltration and three steps of reverse osmosis. This setup (Fig. 1) was chosen according to the process presented by A3 water solutions GmbH [5].



Figure 1: Digestate separation process via solid-liquid separation and membrane purification

For purification costs the calculations made by A3 water solutions GmbH (5,1 \notin t digestate) were considered. In addition, a second scenario with 90% of the purification costs (4,5 \notin t digestate) was calculated, since a decline in costs can be possible because of up-scaling effects.

For the produced fractions (clean process water, solid phase, fertilizer concentrate) neither additional expenses nor financial value was added. The concentrate from ultrafiltration is re-circulated into the process.

3 RESULTS

According to the data of the simulated AD process [1] the amount and characteristics of the digestate could be estimated which would occur at the large-scale bio-ethanol plant. Table I gives an overview of the accumulated loads of nutrients and organic matter.

Table I: Estimated digestate accumulation for AD	of the stillage at the Austrian	large-scale bio-ethan	iol plant
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accumulation (t/yr)				
Total digestate	1,200,000			
COD-Load	35,000			
TKN-Load	7,300			
K-Load	2,200			
P-Load	1,900			

These loads (presented in Table I) were the basis of the calculated economic comparison of the

three digestate treatment options. The outcome of the comparison is presented in Figure 2.



Figure 2: Annual costs in [Mio. €yr] for three different digestate treatment options (for each option two calculated scenarios are presented)

3.1 Application as fertilizer

When the digestate is applied as a fertilizer, a minimum of 36.000 ha of agricultural area would be needed (when fertilizing at a maximum of 210 kg (N).ha-1.a-1). Besides, digestate-storage tanks of about 600,000 m³ would have to be provided. If the application and transportation costs for the digestate are also considered the yearly costs are about 9.5 Mio. \notin yr (see Figure 2). This is the most expensive of the calculated scenarios. On the other hand, if the theoretical fertilizer value (5.4 Mio. \notin yr) is subtracted the annual costs would be less than half as high (4.1 Mio. \notin yr). However, this would mean that the N-, P- and K- loads in the digestate (see Table I) would have the same financial value as commercial fertilizer.

3.2 Aerobic wastewater treatment

For aerobic wastewater treatment the annual costs depend strongly on the addition of the external carbon source. Only two of the calculated scenarios in this option are presented in Figure 2: The cheapest scenario which would mount to 5.2 Mio. \notin yr, where a low ethanol-price was assumed (500 \notin m³) and a low addition ratio of ethanol (EtOH-COD addition to TKN-load is 1:1). The second one was the most expensive scenario which produces costs of 9.4 of Mio. \notin yr. Here a high ethanol-price was assumed (640 \notin m³) and also a high addition ratio of ethanol (EtOH-COD addition to TKN-load is 2:1).

3.3 Membrane purification

The annual costs for membrane purification and solid-liquid separation are about 6.3 Mio. rightarrow (according to the estimations of the manufacturer [5]). When calculating 10% lower costs due to benefits from up-scaling this costs would be reduced to 5.7 Mio. rightarrow (see Figure 2).

4 DISCUSSION

4.1 Application as fertilizer

The application as fertilizer is normally the standard digestate treatment option for AD. This appears to be not possible any more when large amounts of digestate are concerned. In addition, it results to be very expensive because of the cost of storage volume and transportation.

It becomes a competitive option only if the same price (due to its nutrient content) as for commercial fertilizers is paid which is not realistic. To achieve the assumed low transportation cost all the surrounding farmlands are needed for digestate application. Even though the agricultural area needed for the application of animal manure was subtracted, it is still not realistic that the farmers of all the other fields would accept to apply the digestate, especially to pay the theoretical digestate value.

4.2 Aerobic wastewater treatment

When aerobic wastewater treatment is concerned the high nitrogen content is a problem. Therefore, an additional carbon source has to be added which increases the costs. They are about the same or higher than the costs for membrane purification (see Fig. 2).

Using bio-ethanol as carbon source as was done in this study is more a theoretical approach. It does not make sense to produce ethanol where valuable raw materials and a lot of energy is consumed and then to use it for wastewater treatment. This would mean that 2 - 4 % (depending on the calculated scenarios) of the bio-ethanol which is produced at the plant would be needed for aerobic digestate treatment. So cheaper C-sources like stillage or stillage fractions [1] should be considered. However, complications in the purification process like foaming during aeration would be expected. Therefore experiments have to be carried out, to show that a stable process can be achieved.

To buy external C-source would be quite difficult, since large amounts would be needed to treat approx. 100 t per day of COD-load from the digestate. Carbon source in this quantities is normally not available at a cheap price. Only combining the aerobic treatment of digestate with the wastewater treatment of large cities could be a possibility which was not possible at the investigated bio-ethanol plant.

As another option the combination of aerobic wastewater treatment with membrane technology can be a possibility [4].

4.3 Membrane purification

Membrane technology appears to be a desired option for digestate treatment of large-scale biogas plants, since the other two options are either quite problematic or more expensive.

One main advantage of membrane purification is that clean process water can be obtained. This is not the case in the application as fertilizer and after aerobic wastewater treatment an additional cleaning step would be needed to be able to use the purified water as process water.

Another advantage is that a nutrient rich concentrate can be recovered. This can be used as a fertilizer with a higher value than normal digestate and due to higher concentrations the expenses for transportation can be minimized. However, this option is still not without possible disadvantages. First of all the costs have been deduced from experiences in pilot plants, so membrane purification is still no standard technology for digestate treatment. Second, no additional costs for storage, transportation or treatment of the produced digestate fractions were included into the comparison. If the solid residues have to be composted, additional costs would arise. Besides, all the heavy metals and salts accumulate in the concentrate of the reverse osmosis. This could pose a problem for the application as fertilizer of this fraction, especially if biological waste was the substrate for the large-scale biogas plant. On the other hand no financial value was added to the fertilizer concentrate which could different if a market for the fertilizer concentrate can be found. In addition, the solid fraction of the

digestate is rich of phosphorous so it could also be used as fertilizer.

This all shows that still further research is needed in order to establish membrane application in digestate treatment and investigate the remaining doubts.

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Post-treatment methods for groundwater at a former manufactured gas plant (MGP)

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Abstract

Groundwater at a former manufactured gas plant (MGP) in Vienna, Austria, contained high concentrations of hazardous contaminants such as BTEX, PAHs, phenols, cyanide and ammonia. An on-site remediation with a pump-and-treat system significantly reduced effluent concentrations over time (> 99.8 % for BTEX and PAHs). However, the discharge effluent did not meet the legal limits for re-infiltration for some parameters (EPA-16-PAHs, ammonium, nitrite and total cyanide). To address this problem, a polishing pond was operated for 80 days as a simple process step to further reduce chemical concentrations by biological degradation and nitrogen removal. In addition to chemical testing, ecotoxicity tests were conducted on polishing pond effluent using lumistox, Daphnia magna, and algae. Since a biological fixed film reactor was implemented in the preceding P&T plant, the plant effluent was treated with UV irradiation as a mean for bacterial growth control. Post-process chemical analyses showed no significant chemical reduction with the polishing pond, and the ecotoxicity tests exhibited no significant improvements compared to background measurements. Although initial irradiation treatment decreased the colony forming units by 10^{-3} to 10^{-5} , the regermination after 7 days was higher than original pre-treatment conditions, likely due to increased amounts of assimilable organic carbon. Therefore a UV irradiation is not recommended. Although the polishing pond did not significantly reduce dissolved contaminant concentrations, it did produce a functioning habitat with a viable biological community in a relatively short amount of time. The numerous flora and fauna observed in the polishing pond helped convince regulators and community members that the existing P&T system reduced groundwater concentrations at the site to levels that were environmentally acceptable endpoints.

Keywords: Polishing pond, UV-irradiation, Remediation, MGP, Groundwater, Ecotoxicity

1. Introduction

From the nineteenth to mid-twentieth century, gas extraction from coal and oil provided household heat, lightning and industrial fuel (Sanseverino et al., 1993).

Gas production took place at manufactured gas plants (MGPs), which produced relatively large amounts of organic and inorganic waste by-products (Hatheway, 2002). These process byproducts are now an environmental

concern due to their potential for human and ecological risk (Piver, 1992). One of the critical elements that must be addressed at former MGPs is groundwater. Remediation success for MGP-impacted groundwater has been conventionally determined by measuring the total concentration of specific organic contaminants and comparing them against regulatory legal limits. These contaminants typically include polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylene (BTEX), phenolic compounds, and inorganic compounds, such as heavy metals. cyanides, sulfides and ammonium. Other common analyses include sum parameters, e.g. HC-Index, total organic carbon (TOC) or chemical (COD). However, oxygen demand chemical analysis alone may not necessarily be representative of the environmental risk. Therefore. ecotoxicity tests and aquatic biological community data, which theoretically capture true ecosystem endpoints, may provide valuable and complementary information that can then be used to assess overall ecological risks posed by groundwater at the site.

This study evaluated groundwater at a former MGP site in Vienna, Austria, which had already undergone a pumpand-treat (P&T) purification process, comprising of a sedimentation tank, submerged fixed film reactor, multi media filter and finally an activated carbon filter (Wirthensohn et al., 2009).The P&T system had been operated in pilot scale for 6 month. The P&T process is part of a hydraulic management system to avoid migration of the groundwater plume contaminants further down gradient. Most of the treated groundwater is recycled up gradient of the contaminated site through an infiltration gallery. However, part of the pumped water must be discharged into a nearby river to ensure lowering of the groundwater table and overall hydraulic containment.

Therefore two primary concerns arose. First, while the effluent quality was sufficient for direct discharge into the river, several chemical parameters exceeded the set limits for aquifer reinfiltration. A polishing pond was therefore added to the existing P&T system in attempt to reduce these concentrations. However, a second concern was residual bacterial load, since a biofilter was employed in the previous P&T plant. Even if target chemical concentrations were achieved in the polishing pond effluent, it was feared that bacterial activity after reinfiltration might lead to the blocking of infiltration wells. Therefore bacterial growth needed to be prohibited to avoid mechanical failure, and also because the authorities will not allow infiltration of microorganisms into groundwater.

The drawback of several chemical methods for controlling bacterial growth, such as the Fenton reaction or Ozonation, is that they might be biological with incompatible the treatment in the polishing pond or reinfiltration into aquifers. Oxidation techniques can even be harmful to the Biocenosis thev increase the if bioavailability of toxicants (Bhattacharyya et al., 2003). By contrast, no environmentally harmful by-products are produced by Ultraviolet (UV) light irradiation. In addition, photolysis can also decreases the mutagenicity of benzo(a)pryrene by up to two-thirds, as shown by the Ames assay, though it may also increase the acute toxicity (Lehto et al., 2003). Due to these reasons, UV irradiation was selected instead of alternative chemical methods as the primary control for the microorganism density in the polishing pond effluent, despite higher energy demand (Bergendahl et al., 2003).

The scope of the current investigations was several-fold. One aim was to find a cost-effective post P&T process step which might further reduce the level of contaminants in discharged groundwater. A polishing pond was installed because it is relatively inexpensive and has the potential to reduce the contaminant concentrations below regulatory legal limits (Voice et al., 1992). Furthermore the impact of UV irradiation, usually applied for drinking water, was tested on the plant effluent as a bacterial control measure. To evaluate this remedial design, the routine chemical analyses of the water quality were complemented with ecotoxicity testing and aquatic biological community data to evaluate a broader suite of information on the inherent environmental risk. Currently, there is limited information in the peerreviewed literature about the relationship

of these different surveys, especially on fresh water environments.

2. Materials and Methods

2.1 Polishing pond

The dimensions of the polishing pond are presented in Table . The decision for the given hydraulic retention time was based on land availability at the site with regard to the envisaged full-scale process. The inflow to the pond was installed at the bottom, while the effluent was withdrawn near the surface of the opposite side. The pond was planted with reed (*Phragmites australis*), water hyacinths (Eichhornia), water lettuce (Pistia stratiotes) and duck weed (Lemna). After the planting and inoculation of the pond a startup phase of 3 months was allowed, after which samples were collected for 80 d.

In addition to the colonization with various plants, fish were exposed to the polishing pond. These included 2 koi (*Cyprinus carpio*) and 5 grass carps (*Ctenopharyngodon idella*), which were introduced into the pond at the beginning of the 3-month startup period.

Surface Area	16.7 m ²
Depth	0.6 m
Volume	10.0 m ³
Hydraulic Retention Time	48 h
Bottom layer	Gravel, 25-30 mm, 0.2 m height

2.2 Field sampling

The untreated groundwater, treatment plant effluent, and polishing pond effluent were sampled weekly throughout an 80 d period from Aug. 31st until Nov. 24th, 2006. The unstable parameters; pH, dissolved oxygen and specific conductance, were measured in the field using a portable multiparameter instrument (340i, WTW), including ion-specific probes and a specific conductivity meter. The pond water was considered homogenous, since the shallow depth (0.6 m) would not allow a gradient in nutrients or oxygen. The sampling was done weekly or more frequently in medium depth, avoiding suspended solids. All samples were unpreserved and stored at ~4°C until delivered to the laboratory and measured.

2.3 Analytics

2.3.1 Laboratory methods

Concentrations of PAHs were measured with gas chromatography GC-MS Hewlett Packard, HP 6890 using method DIN 38407 F8. Metals were measured with ICP-AES (Jobin Yvon, JY 50P). Samples for total organic carbon (TOC) were analyzed using a Shimadzu TOC-5000A Analyzer.

2.3.2 Microbiological Analysis

Analysis of colony forming units (CFU) for *Escherichia coli*, coliforms and total count (TC) were done by the dilution and spread plate method following the "Standard Methods for the Examination of Water and Wastewater" (APHA-AWWA-WPCF, 1998).

Beside common nutrient agar also R2A nutrient medium was used especially for the determination of the re-germination potential of the water.

The assimilable organic carbon (AOC) was determined according to the method described by van der Kooij (1982). For this method, the samples were inoculated with a mixture of two pure cultures, *Pseudomonas fluorescens P17* and *Spirillum sp. NOX*. The amount of biomass after incubation for 9 days at 15

°C is an indicator for the biological stability of the water.

The re-germination potential is evaluated by the CFU number in 250 ml parallel samples after 7 days incubation in comparison with the starting CFU. To increase the significance, sample analyses were done with plate count (yeast extract) agar at 22°C and 37 °C and with R2A-Medium at 27° C incubation temperature.

2.3.3 Ecotoxicity

The ecotoxicity of the effluent of the P&T system and the polishing pond were evaluated using 3 lines of evidence: bioluminescence, *D. magna* mobility, and algal growth. In order to compare these results against background response, water from the nearby river was also subjected to the same ecotoxicity testing protocols.

<u>Bioluminescence</u>: The Microtox bioluminescence test with luminescent bacteria *Vibrio fischeri* is one of the most recognized, widely used bacterial ecotoxicity test. Acute toxicity is reflected by a decrease in light emission of the bacteria exposed to the test water sample (ISO 11348 Part 1-3, luminescent bacteria test).

Mobility of Daphnia

Daphnia magna Straus are small aquatic crustaceans commonly called "water fleas" which react very sensitive on water contamination. To measure the acute toxicity, Daphnia were exposed to the effluents of the P&T system and the polishing pond, as well as a nearby river and a swimming lake. The mobility of the Daphnia was observed after a 48-h exposure period (ISO 6341; Hund et Traunspurger, 1994).

Inhibition of algae growth

The algal growth tests were performed according to the method OECD 201. An algae suspension was mixed with substrate and brought into microtiter plates. The incubation lasted 72 h at 22°C with a day/night cycle of 16/8 h. The extinction at 485 nm was measured after 0, 24, 48 and 72 h.

2.3.4 UV irradiation

A UV disinfection system for drinking water (WEDECO VISA TSÜ) was installed. The effluent of the P&T system was treated with UV before disposal to the pond. The UV unit emitted UV-C at 254 nm. The dose rate was 22 mWs/cm². Since the turbidity of the P&T effluent was higher than for drinking water, the applied flow rate was lower than usual values for drinking water applications to achieve sufficient dosage. irradiation The resulting exposure time was 18 sec. In addition to these standard conditions, the effects of 3-fold increase and decrease (i.e. 1/3 dose) of the dosage rate were tested by varying the flow rate accordingly, to exposure times of 54 sec and 6 sec, respectively.

2.3.5 Aquatic community survey The biocenosis of the pond was made according to the Saprobien System, an evaluation system of anthropogenic impact on water bodies used in central

Europe. The Saprobien System is similar to the Index of Biological Integrity (USA) or the Index of Stream Condition (AUS). Aquatic life is evaluated on the basis of taxon abundance and taxon ecological sensitivity. These principles are also implemented in the European Union Water framework guideline (Directive 2000/60/EC of the European Parliament, Annex V, 1.1), which comprises an ecological assessment with an emphasis on macrozoobenthos. The Saprobien System classifies water column species and benthic species (sediment inhabiting) into 4 categories according to the water quality of their habitat. Category 1 "oligosaprob" has the highest quality, followed by Bmesosaprob (2) and α - mesosaprob (3), and finally category (4) "polysaprob" has the lowest quality.

3. Results and Discussion

3.1. Groundwater and pump and treat effluent

The effluent quality after the P&T system effluent fulfilled the legal requirements for disposal into public water bodies. Most of the parameters for aquifer re-infiltration were achieved; however, several parameters exceeded the Groundwater Threshold Value Ordinance (PAH, Cyanides, HC, NH₄-N and NO₂-N – see Table 2).

Parameter	Untreated Groundwater	Disposal into public water bodies	Groundwater Threshold Value Ordinance	Pump & Treat Effluent
PAH [µg/l]	$46.7 - 75.0^{a}$	100 ^a	0.1 ^b	<0.10 - 0.29 ^a
Benzene [µg/l]	292.7 - 373.0	-	1.0	< 0.5
BTEX [µg/l]	308.0 - 449.0	100	limited for Benzene and Toluene (1.0; 6.0)	< 0.1
Phenols [mg/l]	0.07 - 0.15	0.1	-	< 0.01
Easy purgable CN ⁻ [mg/l]	< 0.01 - 0.03	0.1	0.03°	< 0.01 - 0.05
TOC [mg/l]	4.8 - 13.0	25	-	3.3 - 7.1
COD [mg/l]	19.7 – 55.2	75	-	11.3 – 14.3
HC [mg/l]	0.12 - 0.54	10	0.06	< 0.1
NH ₄ -N [mg/l]	2.59 - 5.70	10	0.023	4.8 - 7.3
NO ₂ -N [mg/l]	< 0.01	1.0	0.018	0.00 -0.50
Fe [mg/l]	0.18 - 0.72	2.0	-	<0.20 - 0.38
Mn [mg/l]	< 0.02 - 0.25	1.0	-	<0.02 - 0.18
$S_2^{-}[mg/l]$	2.2 - 14.7	2.0	-	< 0.08
PO ₄ -P [mg/l]	< 0.15 - 0.78	2.0	0.06	< 0.15

Table 2: Summary of groundwater chemical concentrations; Austrian legal limits for disposal into public water bodies and aquifers; and effluent chemical concentrations after the P&T system (values in grey fields exceed the Groundwater Threshold Value Ordinance)

^a Sum of 16 PAH congeners according to U.S. EPA

^b Sum of benzo(a)pyrene, fluoranthene, benzo-(b)-flouranthene, benzo-(k)-flouranthene, benzo-(ghi)-perylene, inden-(1,2,3-cd)-pyrene

^c total cyanides

3.2. Performance of the polishing pond

The P&T effluent feeding the pond had stable physical paramaters. The temperature was constantly between 12.7 °C and 13.9 °C, and pH was consistently between 7.2 and 7.5. The dissolved oxygen (DO) was low, and consistently below 0.5 mg/l (Figure 1).



Figure 1: Physical parameters of the P&T effluent (= pond influent)

3.2.1. Chemical Analysis Several parameters were below detection limit before the polishing pond treatment (Benzene, BTEX, Phenols, HC-Index, Sulfide, and Phosphate). Other parameters which were measured above detection limits in P&T effluent showed no significant reductions in concentration following treatment in the polishing pond. Four parameters: COD, Ammonium, Nitrite, and Total Cyanide) exceeded specifications for reinfiltration outside of the hydraulic containment.



Figure 2: Results of analytes measured in P&T effluent and polishing pond effluent. Values shown are average concentrations for weekly measurements made over 80 d.

<u>COD and TOC</u>: Neither COD nor TOC showed a significant change between P&T effluent and polishing pond effluent (Figure 2). It was not possible to analyze which PAHs, hydrocarbons or BTEX contributed to the COD, since they were below detection limit. However, this also means that residual COD was due to unspecific organics, but not the typical MGP contaminants.

<u>Ammonium</u> was expected to be reduced by biological nitrogen removal. Sufficient oxygen was available (av. 3.63 mg/l), due to algae photosynthesis. Also the available nutrients and average pH of 7.49 (miniumum pH = 7.16) should have provided the geochemical conditions appropriate for nitrification (Ahn, 2006). However, only minor reductions were observed. This can be due to the high sensitivity of nitrifying bacteria towards HC (Dawson et al., 2007), even though the residual HC was very low. Another possible explanation is that the hydraulic retention time of 48 h was perhaps insufficient for nitrifying bacteria, which have a doubling time of app. 10 d (Smith et al., 2008). The short retention time was chosen according to the expected groundwater flow to be treated and the available area at the site. A larger pond may have been preferable and achieved different results for nitrification.

<u>Nitrite</u>: The NO₂-N concentration in the pond effluent was significantly higher than in the influent, indicating minor nitrification. Looking at the concentrations of ammonium and nitrate, it must be assumed, that not much nitrification happened. The reason might have been residual HC concentrations and the low HRT, but also the colder temperatures in late autumn. Samples had temperatures between 9.3 and 11.7 °C, while before the lowest temperature was 14.0 °C.

Total Cyanide proved to be a persistent contaminant in the preceding P&T plant, both physical and biological and treatment steps failed to reduce the effluent cyanide concentration, as did granulated activated carbon filter. The polishing pond produced only a minor cyanide reduction (Figure). Similar to other sites, cyanide appeared to be inaccessible any for treatment (Oesterholt et al., 1997). The primary reason for this is that cyanide compounds found at former MGP sites mainly occur as relatively nontoxic ironcomplexed such forms, as ferric ferrocyanide, also known as Prussian blue, which is a widely used as coloring agent, of low toxicity, and highly insoluble (Shifrin et al., 1996).

Chemical analyses may often not be sufficient to estimate environmental risk (Eom et al., 2007), particularly if contaminant bioavailability is not considered by the chemical For example, measurement. in freshwater sediment samples it was samples demonstrated that with hundreds of mg/kg total PAH were not toxic to the sensitive freshwater amphipod, Hyalella azteca. However, by using improved analysis and models, better predictions on the affect of contaminants to these organisms was possible (Hawthorne et al., 2007). And uncertainty always remains due to

complex interactions and because it is not feasible to analyze hundreds of substances. For example, the regulatory based probable effects concentration (PEC) requires 13 PAHs for toxicity estimation while the EPA narcosis model for benthic organisms in polycyclic aromatic hydrocarbon (PAH) requires the measurement of 18 parent PAHs and 16 groups of alkyl PAHs. However, other potential toxicants, e.g. heterocyclic aromatic hydrocarbons, are not listed. Furthermore metabolites of degraded PAHs can be even more toxic than the original compounds. Similar bioavailability arguments apply to total cyanide, which measures all cyanide species and does not account for the toxic fraction of free cyanide, which may constitute <5% of the total at MGP sites (Ghosh et al., 2004). Therefore the chemical measurements were complemented with ecotoxicity tests and benthic macroinvertebrate community analysis to determine whether or not the P&T effluent and polishing pond effluent were producing ecological effects.

3.2.2. Ecotoxicity

The untreated groundwater produced a high inhibitory effect in both the luminescence of *V. fischeri* and the of mobility of *D. magna* tests (Figure 3). There were no significant differences among P&T effluent, polishing pond effluent, and adjacent river for luminescence. For mobility, the P&T inhibition was significantly higher than both the polishing pond and adjacent river water.



Figure 3: Results of two ecotoxicity tests showing the inhibition of Luminescence of *Vibrio fischeri* (left) and Mobility of *Daphnia magna* (right) after exposure to untreated groundwater, P&T effluent, polishing pond effluent, and adjacent river water.

In another attempt to evaluate ecological effects, the impact of effluent on algal growth was investigated, using S. capricornutum and C. vulgaris as test species. The untreated groundwater exhibited a complete growth inhibition for both species. During incubation the amount of algae decreased below the initial level at inoculation. Consequentely the calculated inhibition was higher than 100 %. Interestingly, in certain samples the algal growth was stimulated and the final concentration was higher than for the control sample (i.e. percent inhibition was less than zero) (Figure). The reason for this result is unclear, although the test media contains abundant nutrients which may provide a possible explanation for this stimulatory effect. Similar to the other two ecotoxicity tests above, there were no significant differences among P&T effluent, polishing pond effluent, and adjacent river for inhibition of *S. Capricornutum.* For inhibition of *C. vulgaris*; however, the P&T inhibition was significantly higher than both the polishing pond and adjacent river water



Figure 4: Ecotox test: Algae growth inhibition of S. capricornutum (left) and C. vulgaris (right)

Collectively, the ecotoxicty tests show that the environmental risk was significantly reduced through the P&T system as compared to untreated groundwater. This result is consistent with the reduction in chemical concentration between untreated groundwater and P&T system effluent (Table 2). The percent inhibitions for luminescence and algal growth of *S*.

capricornutum were no different among P&T effluent, pond effluent, and adjacent river (background). However, the reduced mobility of *D. magna* and inhibition of algal growth for *C. vulgaris* showed that the P&T effluent caused a different result than both the pond effluent and adjacent river water. Therefore two of the four ecotoxicity tests appeared to indicate that the polishing pond, which did not

significantly reduce chemical concentrations in the P&T effluent (Figure 2), may have provided some improvement to the overall ecological health of the effluent.

3.2.3. Aquatic biological community Assessment

Table 3: Organsims identified in the Polishing Pond, evaluated using the Saprobien System Classification (1=best, and 4=worst).

English Name	Latin Name	Saprobien Stage
Mollusks		
Freshwater snail	Galba palustris	2 (IS)
Bladder snail	Physa fontinalis	2-3 (IS)
Ramshorn snail	Gyraulus spirillius	2
Insects		
Water strider	Gerris sp	2
Mosquito	Culex sp.	2
Water beetle	Dytiscidae	2-3
Backswimmers	Notonecta glauca	2
Dragonfly	Anisoptera	nR
Mayfly	Ephemeroptera	1-2
(Larvae)		
Soldier fly larvae	Stratiomyidae	3 (IS)
Midge larvae	Chironomus sp.	2-4
Mosquito larvae	Culex sp.	2
Damselfly larvae	Platycnemididae	2 (IS)
Anopheles mosquito larvae	Anopheles sp	2
Backswimmers larvae	Notonecta glauca	nR

(nR=no rating; IS=indicator species)

The aquatic survey recorded a wide variety of zoo benthos in the polishing pond. The indicator species (IS) showed Saprobien System classifications between 2 and 3 (average = 2.3). According to the Saprobien System classification, this translates to a moderately polluted water quality. Unfortunately the Saprobien Index is only an indicator for general impact of

anthropogenic pollution with organic matter. For the influence of toxic system compounds no such is established. In a more typical approach, benthic community analyses are made either by following the structural change in the course of a remediation process or by the comparison of community structure at contaminated and uncontaminated sites. In the investigated case such а profound ecological investigation was not possible, since the polishing pond was an artificial water body. The short duration (3 months startup phase plus 80 d testing period, or ca. 6 months) prohibited the settling of micro flora and micro fauna in balanced quantities, as well as the comparison with an indigenous population. Still a remarkable aquatic life established after only a short duration. It should also be noted that all fish subsisted well in the polishing pond. However, no further investigations or analyses were made on fish.

3.2.4. Microbiology, Control and Conducting the pond



Figure 5: Concentrations of bacteria measured in the P&T effluent and the polishing pond efflucent.

No E. coli bacteria were present in either the P&T effluent or in the pond effluent. This parameter, actually an indicator for fecal contamination, was investigated only because it is a routine parameter in microbiological analyses of water samples and is therefore under strict legal regulation. The less specific fecal indicator, coliform bacteria, was detected in the P&T effluent. It is known that several bacterial species of this group are ubiquitous in the environment with many possible sources. The higher concentrations measured in the polishing pond may have been due to external contamination, for example by birds. These concentrations are above the Austrian limits for drinking water. However, drinking water was not an intended final use of the polishing pond effluent (Figure 5). The Austrian law for groundwater protection (GrundwasserschutzVO, 2000) prohibits the entry of strong oxidants into water bodies and therefore chemical groundwater: oxidation was not an appropriate mean for microbial control. To keep the option for re-infiltration open, a UV irradiation was tested as a final disinfection step between the P&T plant and the polishing pond. Since the P&T effluent had a high turbidity (11 NTU), the transmittance of the UV irradiation was 216 J/m^2 instead

of 400 J/m^2 required for drinking water treatment. Therefore the exposure time was varied and the reduction of total bacterial count was measured at both 22°C and 37°C. The highest TC concentrations were detected in the P&T effluent. Figure 6 shows that the UV irradiation was very effective at reducing concentrations. bacteria At the recommended standard UV dosage rate, no CFU were measured, and at 1/3 of the dose the number of CFU was strongly reduced (Figure 6).



Figure 6: Total bacterial count (left) and bacterial count of indicator organisms (right) in the effluent after the application of increasing UV irradiation rates

Although it has been shown that UV irradiation has no long-term effect on germ reproduction, the formation of bacterial cell debris or the break down of non degradable organic components into easier accessible intermediates may increase the assimilable organic carbon (AOC) and re-germination by microorganisms may occur (Quingrui et al., 1991).

The AOC results showed that with intensification of the UV dose the available organics increased. Interestingly, the AOC reached a maximum at the standard UV dosage rate and decreased at the highest UV dosage rate. This was probably due to

the complete oxidation to inorganic CO_2 at this high dosage rate. These finding confirmed additional was bv investigation addressing the regermination potential (Figure 7 right). Similar findings were obtained by Letho al. (2003),who demonstrated et biodegradation of UV-irridiated anthracene, pyrene benz (a)anthracene and dibenz(a,h)anthracene. The main effect was a reduced lag phase leading to an acceleration of the degradation of PAHs, whereas the final degradation rates were similar for the irradiated and the non irradiated samples. Similar observations were made with chemical techniques: oxidation complex hydrocarbons, such as benzo(a)pyrene were oxidized and the intermediates were better available for degradation which can also enhance re-germination.

In consequence, UV irradiation can be seen as an efficient tool for disinfection,

but bacterial re-growth will rapidly occur. Hence it is questionable whether the desired effect, i.e. the minimization of the risk of well clogging, can be achieved.



Figure 7: Assimilable organic carbon (left) and re-germination potential (right) in the P&T effluent after the application of increasing UV irradiation rates

4. Conclusions and Recommendations

The polishing pond used in this study produced no significant contaminant reductions in the P&T system effluent. The P&T system included an activated filtration, which produced carbon effluent concentrations that were low and often below detection limits for many common MGP parameters. A suite of ecotoxicty tests showed that the environmental risk was significantly reduced through the P&T system as compared to untreated groundwater. However, two of the four ecotoxicity tests appeared to indicate that the polishing pond may have provided some improvement to the overall ecological health of the effluent. Employed at the end stage of a P&T process, the polishing pond proved to be a reliable, low-cost process step for improving the remedial design. Further investigations

with UV irradiation to decrease the bacterial count in the P&T effluent demonstrated high efficiency, but the initial effect was not sustainable, and bacterial growth quickly re-initiated. This effect would likely stimulate biological clogging of infiltration wells when effluent is re-injected, and therefore UV irradiation is not recommended.

Even though only minor contaminants removal was achieved in the polishing pond, it proved to be useful as an instrument for "biological monitoring": an impressive diversity of aquatic life developed within short time and made the achievement of a good groundwater remediation visible for regulators and non-experts alike. This result can be important to meet third party issues at remediation projects. Former MGP sites are located mostly in central and densely populated areas, and the ultimate remedy selection is often dependent upon public acceptance.

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