IMF IMMERSED MEMBRANE FILTRATION

# Preliminary Studies on P-removal by Adsorption from MBR filtrates

- final report -

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## Abbreviations and Notations

| | |
|---|---|
| $BT_{st}$ | stoichiometric breakthrough [BV] |
| BV | bed volume [L] |
| c | liquid-phase concentration [mg/L] |
| $c_0$ | initial (batch) or influent (continuous) liquid-phase concentration [mg/L] |
| $c_{eq}$ | liquid-phase equilibrium concentration [mg/L] |
| DM | dry mater |
| DIC | dissolved inorganic carbon |
| DOC | dissolved organic carbon |
| EBCT | empty bed contact time [min] |
| L | liquid volume [L] |
| m | mass of sorbent [g DM] |
| MBR | membrane bioreactor |
| o-P | ortho-phosphorus |
| P | phosphorus |
| q | solid-phase concentration [mg/g DM] |
| $q_0$ | solid-phase concentration at equilibrium with $c_0$ [mg/g DM] |
| Q | volumetric flow rate [L/min] |
| $\rho$ | density [g/L] |
| SAC | spectral absorption coefficient |
| TIC | total inorganic carbon |
| TOC | total organic carbon |
| t-P | total phosphorus |

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# 1 Introduction

In general and especially in Berlin the nutrient phosphorus (P) is a decisive parameter for eutrophication of receiving water courses. Future stringent phosphorus regulations are expected for wastewater discharge, which can go down to 50 µg/L P. The cost effective and efficient advanced phosphorus removal is studied in membrane bioreactors (MBR) for decentralized wastewater treatment plants by a project conducted in the frame of the Competence Center Water of Berlin and financed by Berliner Wasserbetriebe and Vivendi Water. The enhanced biological phosphorus removal in investigated in MBR at the site of the municipal wastewater plant Berlin-Ruhleben. In the scope of this IMF-project (Immersed Membrane Filtration) an additional P-removal step by adsorption was investigated here to a previous treatment in MBR with simultaneous precipitation and/or enhanced biological phosphorus removal. The basis for evaluation of all three P-removal processes are costs and achievable effluent concentrations.

The aim of this study is to offer a post-treatment step to guarantee stringent effluent criteria in the scope of optimizing the advanced phosphorus removal in MBR with immersed membranes. Hereby, the advanced P-removal from particle-free MBR filtrates is further enhanced by means of fixed bed adsorbers filled with different sorbents. The particle-free MBR filtrates have the advantage of no particle accumulation in the sorption filters.

In general, different commercially approved and new sorbents can be used for P-adsorption. One of the new materials is granulated ferric hydroxide (GFH; $\beta$-FeOOH), which was developed in the Department of Water Quality Control a few years ago and is used technically for the removal of phosphorus and arsenic.

GFH and two other suitable sorbents, activated alumina (ATE) and a poorly known iron hydroxide/oxide (FER), were tested in these trials for the most important characteristics of P-removal processes from MBR filtrates by preliminary bench scale tests and small sorption filters.

Phosphorus sorption isotherms are investigated to determine the capacity and affinity of different sorbents for P-sorption. A competition by other water constituents (organics, sulfate etc.) was studied to assess any effect on P-loading. Subsequently the breakthrough behavior of phosphorus and other constituents was examined in fixed-bed columns in continuous flow mode.

A reuse of sorbents is envisaged after regeneration of loaded adsorbers. Sodium hydroxide might be a sufficient regenerate for most sorbents. In the case of GFH an oxidative regeneration with hydrogen peroxide is also studied. Hereby, sorbed organics are chemically oxidized and therefore adsorption capacity is improved for P-removal.

Finally, based on these results first conclusions will be drawn on the estimated costs of sorbent applications including the reuse of sorbents. The aim is an optimized, cost-efficient sorption process for the advanced treatment of membrane filtrates with P-removal.

## 2 Material and methods

In the following, first the filtrates from membrane bioreactors used in these trials are characterized. Afterwards the chemical-physical properties of the three sorbents are described followed by the experimental set-up and analyses used.

### 2.1 Filtrates from membrane bioreactors

MBR filtrates from two different plants were used, which were run for enhanced phosphorus removal parallel to the municipal wastewater plant Berlin-Ruhleben. A MBR bench-scale plant (BSP) of 200-250 L volume were operated by the Institute of Chemical Engineering of the TU Berlin (Adam et al., 2001) under a sludge age of 15 days. Two MBR pilot plant PP1 and PP2 (1-3 $m^3$ volume each) were continuously run at a sludge age around 26 days (Gnirss et al., 2002). In most cases, MBR filtrates from PP 2 were investigated containing no or very low nitrate concentrations due to post-denitrification.

The filtrates from the bench-scale plant were withdrawn between July 4th and Oct. 4th 2001 and used for the determination of most isotherms and batch-experiments. Exclusively the breakthrough of adsorbers were investigated by filtrates from the pilot plant of the period Oct. 25th 2001 to Feb. 7th, 2002. **Table 2.1** gives an overview of chemical parameters in filtrates from both plants in the period studied.

The dissolved organic carbon (DOC) concentration ranged from 9 to 17 mg/L. Additionally, the organic compounds are characterized by the spectral absorption coefficients at 254 nm ($SAC_{254nm}$), where organic substances containing double bonds or aromatic systems absorb, and at 436 nm ($SAC_{436nm}$) representing the yellow color of filtrates. Major differences can be stated in the dissolved inorganic carbon (DIC) between both plants. Around pH 8 hydrogencarbonate is the predominating species representing DIC. The cause probably lies in differences in the aeration systems of both MBR reactors.

The higher ortho-phosphorus concentration was caused by spiking the influent of the bench-scale plant. Due to membrane pore sizes of 0.07 µm and 0.2 µm particulate phosphorus can be neglected here. Therefore in both plants the concentrations of total and ortho-phosphorus were nearly the same. While the chloride and sulfate concentrations were around 100 to 270 mg/L, the nitrate concentration ranged from zero up to 26 mg/L depending on using post- or pre-denitrification as operation mode in each plant.

**Tab. 2.1:** Chemical parameters of MBR filtrates from the bench-scale plant and pilot plant in the studied period.

| **Parameter** | **Bench-scale plant (BSP)** | **Pilot plant (PP)** |
|---|---|---|
| **DOC [mg/L]** | 9.9 - 14.6 | 9.3 - 16.7 |
| **DIC [mg/L]** | 28.8 – 46 | 43.6 – 72.4 |
| **$SAC_{254\ nm}$ [$^1/_m$]** | 24.5 – 35 | 26.2 – 30.7 |
| **$SAC_{436\ nm}$ [$^1/_m$]** | 1.2 - 2.9 | 1.2 - 1.9 |
| **$Ca^{2+}$ [mg/L]** | 84.2* | 119.6 - 140.4 |
| **$P\text{-}PO_4^{3-}$ [mg/L]** | 0.1 - 8.2 (11.6) | 0.008 - 0.23 |
| **$P_t$ [mg/L]** | 0.1 - 8.5 | 0.03 - 0.27 |
| **$Cl^-$ [mg/L]** | 102 – 265 | 160 – 212 |
| **$NO_3^-$ [mg/L]** | 9.4 - 25.6 | 0 - 24.2 |
| **$SO_4^{2-}$ [mg/L]** | 96 – 181 | 123 – 169 |
| **pH [-]** | 7.9 - 8.4 | 7.9 - 8.7 |

* one value measured. The low concentration is probably effected by precipitation with spiked P within the BSP.

The mean calcium concentration of the filtrates is very similar to drinking water in Berlin. Only one calcium value was measured for the BSP, which is relatively low and may be effected by spiking the influent of BSP to a high phosphorus concentration resulting in partial precipitation of calcium phosphate compounds. Routinely the used filtrates were scanned in a spectral photometer over the whole wavelength range (190-790 nm; Lambda 12 UV/VIS-spectrophotometer, Perkin-Elmer) and featured no differences in bench-scale and pilot plant down to 210 nm.

## 2.2 Sorbents

Three different sorbents were screened and assessed for P-removal, which all consist of metal hydroxide/oxides (see **Table 2.2**). Granulated ferric hydroxide (GFH; $\beta$-FeOOH, akaganeite) was developed for drinking water treatment a few years ago (Driehaus, 1994) and is used technically for the removal of arsenic. The oxidative regeneration of GFH was developed successfully for the treatment of textile wastewater within the Cooperative Research Center Sfb 193 “Treatment of industrial wastewater” in the Department of Water Quality Control at the TU Berlin (Kornmüller et al., 2000, 2001). Earlier fine grained activated alumina (ATE; $\gamma$-$Al_2O_3$) has been applied in stirred reactors with secondary effluents for phosphorus removal in the municipal wastewater plant Berlin-Ruhleben (Donnert, 1988). FerroSorp®Plus is a new product of the company Hego Biotec (Berlin) and was not well-known up to these trials. It represents a mixture of iron hydroxides and oxides containing only 45 % of ferric ions. The data of all three sorbents and their physico-chemical properties are given in **Table 2.2**.

**Tab. 2.2:** Data of the three sorbents used in these trials (manufacturers instructions)

| | **GFH (GEH Wasser-chemie)** | **ATE COMPALOX® AN/V-801 (alusuisse martinswerk)** | **FER FerroSorp® Plus (HeGo Biotec GmbH)** |
|---|---|---|---|
| **composition** | 100 % $\beta$-FeOOH (techn. quality) | 90 % $\gamma$-$Al_2O_3$,<br>0.35 % $Na_2O$,<br>0.01 - 0.03 % CaO, 0.01 - 0.03 % $Fe_2O_3$ | mixture of $Fe(OH)_3$ and $Fe_2O_3$*$XH_2O$, 45 % $Fe^{3+}$, bonding agent (org.) |
| **specific surface area [m²/g]** | 280 | 230 - 300 | 300 |
| **particle size [mm]** | 0.32 - 2 | 0.3 - 1 | 0.8 - 2 |
| **water content [%]** | 43 | 0.4 | 3.2 |
| **bulk density [kg/m³]** | 1250 | 900 | 750 |
| **price [EUR / t]** | 4200 | 1200 | 1500 - 2000 |

For all sorbents the specific surface area is around 300 m²/g, while their particle size distribution differs. ATE includes the finest grained particles from 0.3 - 1 mm, while the particle size of FER is very coarse. GFH has a wide particle size distribution covering the whole range. In the case of GFH, the water content has to be taken into account for process design, which can be neglected for the other two sorbents. GFH features the highest material price followed by FER and ATE.

## 2.3 Experimental set-up

### Sorption isotherms

For determination of sorption isotherms, ATE and FER were ground in a mill and sieved to a fraction < 63 µm. Because dried GFH will lose its capacity and to avoid high temperatures in a mill, GFH was dosed from a stock suspension (40 g/L) first. Later a preparation process was developed including drying at room-temperature, grinding per mortar and sieving to the fraction < 63 µm (water content ~22 %). No loss in capacity could be observed in this room-dried ground GFH compared to the use of suspension. In contrast, the use of suspensions effected more variations in isotherms due to the problem of homogenous dosing. To evaluate adsorption isotherms, the method of adding different quantities of sorbent (m) to solution volumes (L; L/m variable) of the same initial concentration ($c_0$= const.) was used. Defined quantities of sorbent (m= 10 - 1000 mg DM) were added to several glass bottles containing defined volumes of MBR filtrate (L= 250 mL). Depending on their P-concentration, original or previously spiked MBR filtrates were used. The initial concentration ranged from 4-12 mg/L P. For spiking P-buffer solutions ($Na_2HPO_4$, $KH_2PO_4$) were used retaining the original pH of MBR filtrates. The flasks were stirred for at least 96 h at 20 °C. The loading q in dependence on the reached equilibrium concentration was calculated using **Equ. (2)** (**chapter 2.5**).

### Differential recirculating flow reactor

The differential recirculating flow reactor was used for kinetic experiments and for regeneration studies of technical sorbents. Its set-up and experimental conditions are shown in **Figure 2.1**.

From a well-mixed storage tank the P-spiked MBR filtrate was cycled over a bed containing a thin layer of sorbent particles under defined flow conditions and room-temperature (~ 20°C). Samples were taken out of the storage tank for analyses. This set-up can be modeled as a completely mixed batch-reactor (Sontheimer et al., 1988).

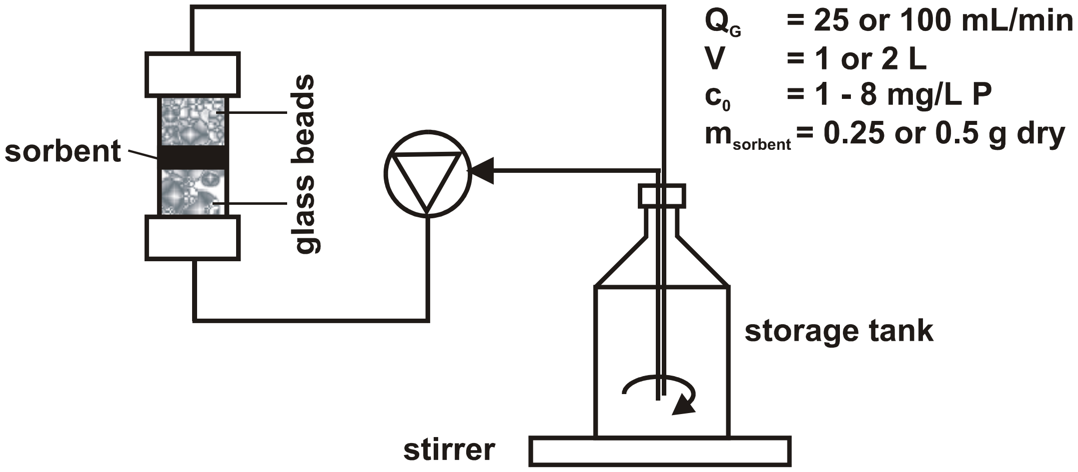

**Fig. 2.1:** Differential recirculating flow reactor for kinetic and regeneration experiments.

For regeneration experiments fresh sorbents were first loaded in differential recirculating flow reactors for a defined time by cycling 2 L MBR filtrate with an initial P-concentration of 4 mg/L. Then loaded columns were regenerated by cycling 0.6 M NaOH, 2.8 M NaOH or 3% $H_2O_2$-solution for 17 h or 68 h. For reconditioning columns were rinsed with deionized water and the pH adjusted to neutral region again before reloading. Blind columns were run in parallel without regeneration to assess still existing adsorption capacity in reloading.

### Filter breakthrough tests

A preliminary filter breakthrough test was conducted in small sorption filter in columns of 2.5 cm diameter and 2 cm height. A short empty bed contact time EBCT of 10 min was used, which was equivalent to a through-put of six bed volumes per h. These trials were performed with MBR filtrate from the bench-scale plant spiked to 8 mg/L P for seven days. All three sorbents were tested in their technical particle size.

For advanced filter breakthrough tests larger columns were chosen (diameter 2.5 cm, height 20 cm), which were equipped with five samplers over the height referring to different real EBCT from 3 to 36 min and through-puts of 1.6 to 17 BV/h (see **Figure 2.2** for mean construction parameters). Columns filled with GFH and ATE were run in parallel, each fed downstream by MBR filtrates with spiked influent concentrations of 0.1 and 0.3 mg/L P at room temperature (18-25 °C) from Oct. 31th, 2001 to Feb. 7th, 2002. To prevent algae growth the columns were shaded. Before loading the GFH columns were backflushed upstream to remove any air bubbles left in the bed by filling according to the manufacturers instruction.

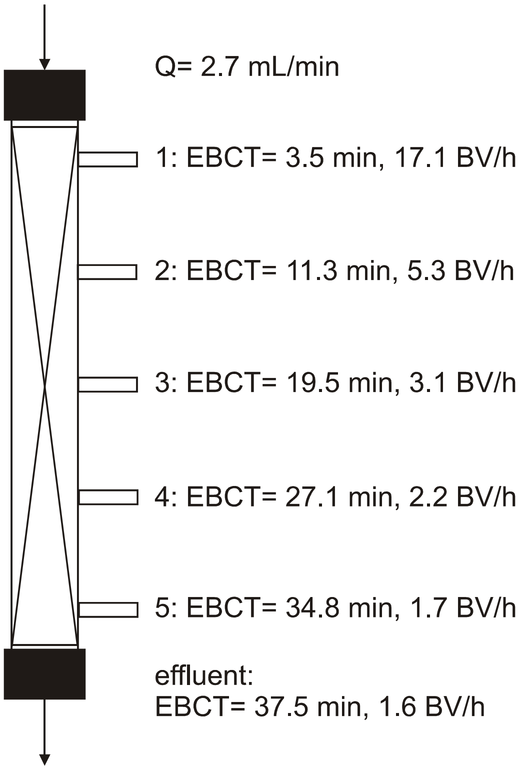

**Fig. 2.2:** Mean construction parameters of filter columns in larger scale for studying breakthrough behaviors.

## 2.4 Analyses

### Sample preparation

For exemption from P all glassware were stored in an acid bath overnight and rinsed with millipore®-water. For isotherms initial and equilibrium samples were filtered by 0.45 µm cellulose-nitrate-filter. Samples were kept at 10°C until analyses.

### Ortho- and total phosphorus

Ortho-phosphorus (o-P) was determined by the ammonium molybdate spectrometric method according to the German version EN 1189 : 1996. The formed blue complex was detected at a wavelength of 880 nm using a Lambda 2 spectrophotometer (Perkin-Elmer). For total-phosphorus (t-P) analyses the samples were first pulped in an autoclave with $K_2S_2O_8$. Measuring ranges of 5 - 500 µg/L and 0.125 – 1 mg/L o-P were used. The concentrations are always given as phosphorus in mg/L P.

Since Dec. 20th, 2001, a flow injection analyzer (FIAstar 5000, Foss Tecator) was used according to ISO/DIS 15681 : 2001 part 1. The analysis bases on a formation of heteropolyacids in the presence of phosphate and molybdate ions in acidic solution, which are reduced in a second step by tin(II)chloride to a blue colored molybdate complex. Measuring ranges of 0 - 500 µg/L and 0.1 – 5 mg/L P were utilized.

Especially in the lower P-concentration range the flow injection analyzer revealed a better standard deviation of 4.8 % at a mean concentration of 0.016 mg/L P and 0.77 % at 3.8 mg/L, while with spectrophotometer the standard deviation amounted to 6.1 % at a mean concentration of 0.085 mg/L and to 1.25 % at 11.7 mg/L P. The detection limit of the flow injection analyzer is around 3 µg/L and of the photometer method 5 µg/L P.

### Spectral absorption coefficient

Spectral absorption coefficients SAC at 254 nm and 436 nm [1/m] were determined using a Lambda 12 UV/VIS-spectrophotometer (Perkin-Elmer) and cuvettes of 1 cm length.

### DOC/TOC and DIC/TIC

Dissolved organic carbon (DOC) or total organic carbon (TOC) and dissolved inorganic carbon (DIC) or total inorganic carbon (TIC) were analyzed undiluted by thermal-catalytic oxidation using a highTOC analyzer (elementar Analysensysteme). For determination of isotherms the samples were filtered giving the DOC, while samples were not filtered from the continuously operated sorption filters giving the TOC. Due to the membrane cut at $\leq$ 0.2 µm the TOC and DOC are nearly the same with the exception of later contamination.

### Ionic chromatography

Chloride, nitrate and sulfate were analyzed by a Dionex DX500 ion chromatograph with an Ionpac AS11 analytical column and a CD20 conductivity detector. Filtered samples were diluted 1:10 and 25 µL were injected. The eluents used consist of UV-oxidized deionized water from an ELGA unit, 5 mM NaOH and 100 mM NaOH. At a flow rate of 2 mL $\text{min}^{-1}$ a gradient program was applied for separation.

### Calcium

Calcium was determined by atomic absorption spectroscopy (Varian Spektra AAS 300) at the wavelength of 422.7 nm according to DIN 38 406 – E3-1 (Sept. 1982). Due to the measuring range up to 6 mg/L samples had to be diluted by 1:20 or 1:40.

### pH

The pH was measured by a WTW pH 340-meter using a Sentix 41-electrode (WTW).

## 2.5 Equations

### Empty bed contact time

The empty bed contact time EBCT [min] of a sorption filter is defined as:

$$EBCT = \frac{BV}{Q} \tag{1}$$

with BV: bed volume [L] and Q: volumetric flow rate [L/min].

### Sorption equilibrium

The sorption equilibrium follows from the mass balance of the system:

$$q = \frac{L}{m}(c_0 - c_{eq}) \tag{2}$$

with q: solid-phase concentration [mg/g DM], $c_0$: initial liquid-phase concentration [mg/L], $c_{eq}$: liquid-phase concentration [mg/L] at equilibrium, L: liquid volume [L] and m: mass of sorbent [g DM].

### Stoichiometric breakthrough

From isotherms the stoichiometric breakthrough $BT_{st}$ [BV] at a certain bed volume (BV) of sorption filters can be calculated by:

$$BT_{st} = \frac{q_0 * \rho_m}{c_0} \tag{3}$$

with $q_0$: solid-phase concentration at equilibrium with $c_0$ [mg/g DM], $c_0$: liquid-phase influent concentration [mg/L] and $\rho_m$: density of sorbent [g/L] (for GFH the dry-matter density has to be used in **Equ. 3**)

## 3 Results and discussion

First sorption isotherms were determined to assess the capability of all three sorbent in P-removal from MBR filtrates. Potentially influencing parameters (like pH, T, other constituents) were studied to detect most important characteristics and reveal possible competition in P-sorption. Subsequently, the breakthrough behavior of P and other constituents were investigated in fixed-bed adsorbers filled with the different sorbents in continuous operation in the lab. Finally, the regeneration of loaded sorbents was studied in differential recirculating flow reactors for reloading and reuse of sorbents. By these bench-scale and preliminary filter tests first estimations on costs were drawn assuming different scenarios.

### 3.1 Sorption isotherms

By sorption isotherms the affinity of constituents in the MBR filtrates was determined to different sorbents and the sorbent with the highest capacity for phosphorus was assessed. Additionally, the stoichiometric breakthrough in fixed-bed sorption filter can be estimated from isotherms.

### 3.1.1 Capacity and affinity

First the capacity of all three sorbens was studied in different MBR filtrates from the bench-scale plant (BSP). **Figure 3.1** shows the loading given as mg P per mg dry matter (DM) of sorbent versus equilibrium concentrations in mg/L P. Hereby, every point of the isotherm is a single batch.

The highest loading and therefore capacity in P-removal is achieved by GFH followed by ATE and FER. For an efficient treatment a high affinity to phosphorus of sorbents is required, which is tantamount to already high loadings at low equilibrium concentrations. GFH shows the highest affinity likewise: at a P-equilibrium concentration of 0.5 mg/L the loading on GFH amounts to 20 mg/g, on ATE to 9 mg/g and on FER only to 3.8 mg/g.

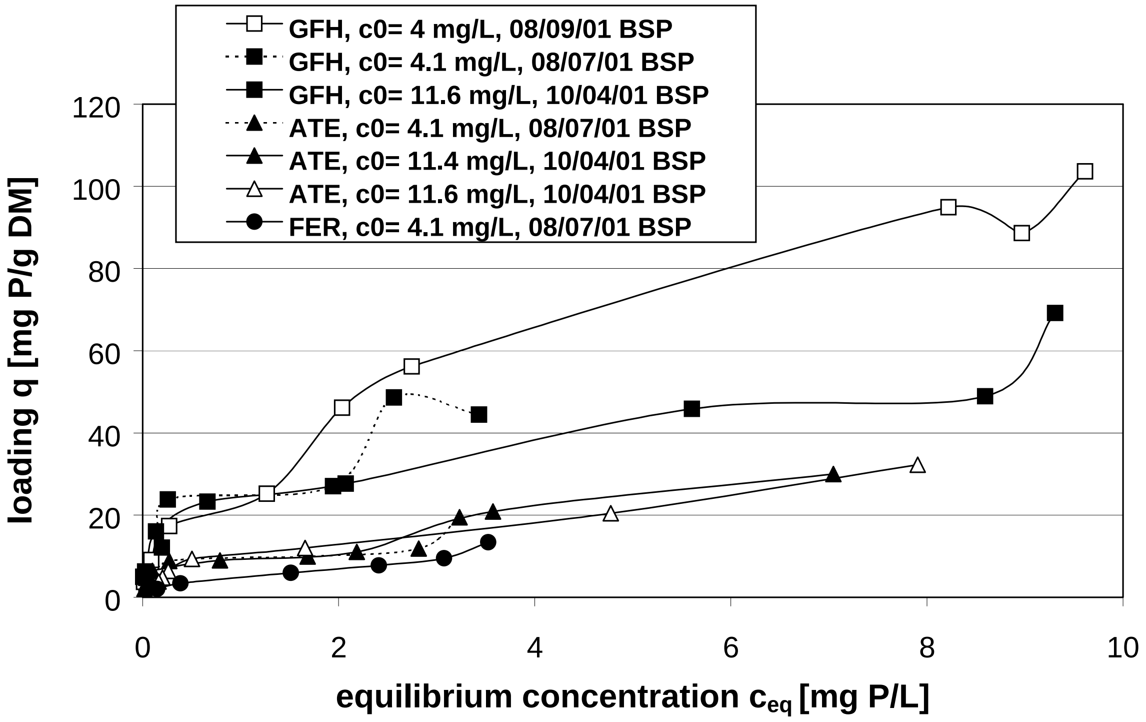

**Fig. 3.1:** Isotherms of phosphorus on GFH, ATE and FER using different initial P-concentrations at pH 8.2 ± 0.25.

Whenever the equilibrium concentration becomes near to the initial P-concentration $c_0$ a steep increase in isotherms and greater fluctuations in loading can be recognized. At this equilibrium concentration range a high volume/mass ratio is used in determining isotherms. Therefore, little variation in the sorbent mass, which is very low here (down to 10 mg), effects already larger changes in loading (compare **Equ. 2**). Additionally, the standard deviation of P-analyses has to be taken into account. However, its influence is rather low, because the standard deviation amounts to less than 1.5 % at high P-concentration (see **chapter 2.4**).

In general, different P-elimination processes like biodegradation and precipitation can occur besides sorption. A biodegradation might be possible even in MBR filtrates, because they do not have to be sterile. MBR filtrates can be contaminated by tear-off of membrane hollow fibers in reactors or by the environment at the plant. Also a few microorganism are known to be able to pass even membranes with a cut of 0.1 µm like Spirochaeten (personal information by Prof. Szewzyk, TU Berlin). Therefore, biodegradation was checked by stirring different unspiked and spiked MBR filtrates without sorbents, which were not filtered or supplementary filtered by a 0.1 or 0.2 µm membrane filter to increase removal of possible microorganism. No differences between these batchtests could be detected indicating that biodegradation as an additional P-removal process can be neglected here. But in the spiked filtrates ($c_0$= 10.8 – 12 mg/L P) phosphorus concentrations started to decrease above 50 - 70 h to 24 - 58 % of the initial P-concentration at 236 h. At pH 8.5 the precipitation of different calcium phosphate compounds is possible here.

In general, the literature is very inhomogeneous concerning conditions for precipitation of calcium phosphate compounds. Calcium forms several insoluble phases with phosphate, from which a few solubility products are known like from calcium hydrogen phosphate $CaHPO_4$ to the thermodynamically stable end product hydroxyapatite $Ca_5(PO_4)_3OH$ (Leckie and Stumm, 1970; Mauer et al., 1999). In spiked MBR filtrates a precipitation of these calcium phosphate compounds is possible above pH 8, but precipitation is known to be slow and instable under these conditions. While the precipitation of calcium phosphate compounds is possible in MBR, the phosphate precipitation can be neglected by other metal cations (Al, Fe, Mg) due to their concentrations, which are already in the influent of the municipal wastewater plant Berlin-Ruhleben lower than the calcium concentration (Künert, 2001).

Therefore, in the determination of isotherms, where MBR filtrates have to be spiked by P to obtain sufficient loadings, precipitation has to be considered as an additional P-elimination mechanism at high equilibrium P-concentrations. Hereby, it can not be distinguished between a precipitation of P in water or at the interface solid/water, where a higher calcium concentration has to be assumed due to co-sorption (see **chapter 3.1.6**).

From **Figure 3.1** it becomes also obvious, that an additional elimination to sorption depends on the kind of MBR filtrate used. The MBR filtrate from the bench-scale plant dated 10/04/01 had a very high P-concentration of 10.6 mg/L, which was effected by spiking the influent of MBR to a concentration of 40 mg/L. In this case, all removable phosphorus was already precipitated within the bench-scale plant. Due to the high effluent P-concentration of the plant is was not necessary to spike this MBR filtrate further for isotherm trials here. Until an equilibrium concentration of 8 mg/L no indications on precipitation during the sorption experiments can be detected in this case, while in MBR filtrates dated 08/07 and 08/09/01, which were spiked around

4 mg/L phosphorus, an additional precipitation is already likewise at equilibrium concentrations above 2 mg/L. Especially in the case of GFH, a steep increase in the isotherm is already recognized at equilibrium concentration ≥ 2 mg/L indicating that a surface precipitation might be initiated by the sorbent itself.

It has been shown that conventional activated sludge plants with Bio-P reach P-effluent concentrations < 1 mg/L, e.g. in the municipal wastewater treatment plant Berlin-Ruhleben << 0.5 mg/L. In the scope of the IMF-project the effluents of MBR-pilot plants lie below 0.3 mg/L, which might be attributed to the complete removal of particulated phosphorus and the higher sludge ages compared to conventional plants. Therefore, only the lower P-concentration range is relevant for the adsorption process. Additionally, an influence by precipitation could be excluded for equilibrium P-concentrations below 2 mg/L, because sorption is much faster than precipitation at low volume/mass ratios and P-isotherms in calcium free millipore®-water gave similar loadings as in MBR filtrates here. Therefore, the following experiments concentrate on equilibrium and influent P-concentrations below 2 mg/L. At low influent resp. equilibrium concentrations the high affinity of sorbent becomes especially relevant for P-removal. Due to the first results with Bio-P in MBR, the cost calculation will be done for influent concentrations of 0.1 and 0.3 mg/L to the sorption process (**chapter 4**).

According to **Equ. 3** the stoichiometric breakthrough of sorption filters can be calculated from isotherms. In **Table 3.1** the corresponding values are given for liquid-phase influent concentrations of 0.1 and 0.3 mg/L P and zero effluent concentrations in sorption filters considering the loadings from isotherms.

**Tab. 3.1:** Calculation of breakthrough points at two different influent concentrations for all three sorbens (BV= 90 mL; compare Equ. 3).

| | **$c_0$= 0.1 mg/L** | **$c_0$= 0.3 mg/L** | | | **$c_0$= 0.1 mg/L** | **$c_0$= 0.3 mg/L** | **$c_0$= 0.1 mg/L** | **$c_0$= 0.3 mg/L** |
|---|---|---|---|---|---|---|---|---|
| **Sorbent** | **$Q_0$ [mg/g DM]** | | **ρ [g/L]** | **m [g]** | **Q treat. [L]** | | **breakthrough at BV** | |
| **GFH** | 10 | 18 | 525* | 47.25 | 4,725 | 2,835 | 52,500 | 31,500 |
| **ATE** | 5 | 7 | 900 | 81 | 4,050 | 1,890 | 45,000 | 21,000 |
| **FER** | 1,7 | 3 | 750 | 67.5 | 1,148 | 675 | 12,750 | 7,500 |

* The water content of GFH is considered here.

For an influent concentrations of 0.3 mg/L P a through put of 31,500 bed volumes (BV) would be theoretically possible until complete saturation, while for ATE the breakthrough can be estimated to appear after 21,000 BV and for FER after 7,500 BV. These estimated values can be compared with the data evaluated by the performance of these sorbents in fixed-bed sorption filters described in **chapter 3.2**.

### 3.1.2 Removal and presence of organics

Besides the P-removal an elimination of organic compounds is aspired from MBR filtrates by sorption. Especially the yellow color is objected in MBR filtrates. In **Figure 3.2** the equilibrium concentration of dissolved organic carbon (DOC) is shown in dependence on the sorbent mass in each batch.

GFH is known to be a moderate sorbent for dissolved organic carbon. Like for phosphorus, GFH features the highest capability to remove organics compared to ATE. In contrast, no DOC-removal is obtained by FER and even a small increase in DOC can be stated.

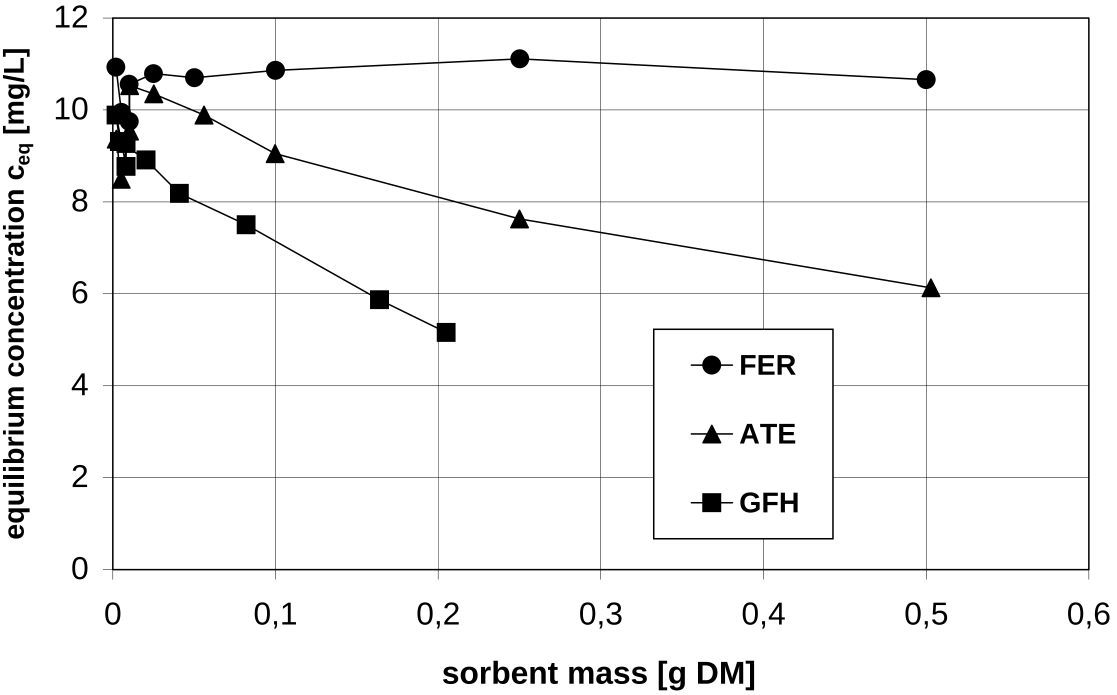

**Fig. 3.2:** Equilibrium concentration of dissolved organic carbon versus sorbent mass of GFH, ATE and FER (MBR filtrate, pH 8.3).

In addition to DOC, the UV absorbance at 254 nm indicates organic compounds containing double bonds. The yellow color can be detected at the typical wavelength 436 nm. In **Figure 3.3** the spectral absorption coefficients SAC of these both wavelengths is given in dependence on sorbent mass. The ability of GFH to remove the yellow color at SAC 436 nm is striking compared to both other sorbents. Again FER is not capable of removing organics at all. In contrary, again an increase can be recognized here at SAC 254 nm. The increase in organic equilibrium concentration with rising FER mass is probably caused by desorption of an organic bonding agent used in production of FER. Together with the small P-sorption capacity (see **Fig. 3.1**) this was the reason, why the trials with FER were not considered anymore.

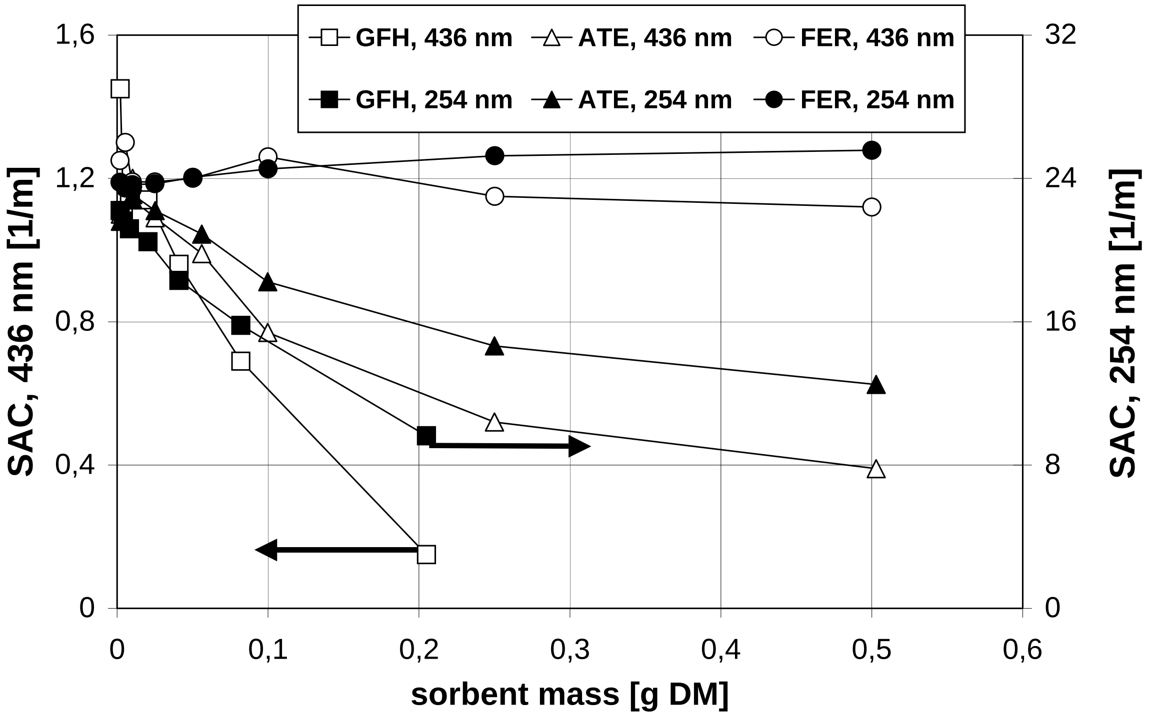

**Fig. 3.3:** Spectral absorption coefficients SAC at 254 nm and 436 nm versus sorbent mass of GFH, ATE and FER in equilibrium (MBR filtrate, pH 8.3).

Altogether, GFH and ATE possess partial capacities to remove DOC besides phosphorus in the MBR filtrates.

In unspiked MBR filtrates the DOC-concentration is around 50 times higher than the P-concentration (compare **Tab. 2.1**). As the DOC can not be attributed to a single compound, its influence on P-sorption can not be evaluated by spiking. But a comparison of simultaneous P- and DOC-isotherms in MBR filtrates (**Figure 3.4**) reveals their different positions in dependence on equilibrium concentrations.

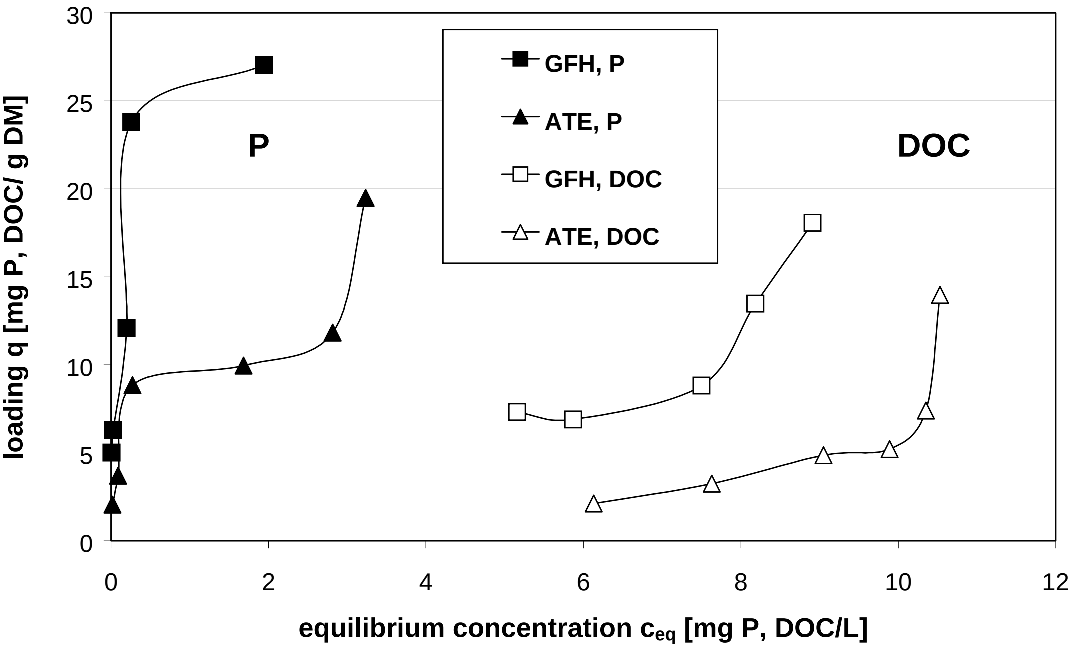

**Fig. 3.4:** Simultaneous P- and DOC-isotherms on GFH and ATE (pH 8.4).

Both sorbents GFH and ATE have a higher affinity to P-sorption than to DOC-sorption, which is especially important at low effluent P-concentrations from MBR resp. equilibrium P-concentrations. As discussed, DOC can only be removed partially by both sorbents. Therefore, from these DOC-isotherms an effluent concentration of 5 - 6 mg/L DOC is immediately expected in sorption filters. Nevertheless, from studying the filter breakthrough behavior (see **chapter 3.2**) it becomes obvious that DOC is the only constituents of MBR filtrate most likely being capable to compete for sorption sites.

### 3.1.3 Influence of pH

In the literature the sorption mechanism onto alumina oxide can be viewed comparably to the one to ferric hydroxide, like GFH. In both cases, the metal hydroxide/oxide surface is hydrated in equilibrium with water and protonation and deprotonation of hydroxide groups at the metal surface takes place depending on pH. Therefore, the surfaces are positively charged at acidic pH and a better anion sorption is expected. Consequently **Figure 3.5** shows a higher P-loading on GFH and

ATE for pH around 5.5 compared to pH above 8. But the gain in sorption capacity of up to 30 % is rather small by decreasing pH. Due to the strong buffering of MBR filtrates by the carbonate/hydrogencarbonate system, the pH-influence has only theoretical significance for P-sorption from MBR filtrates.

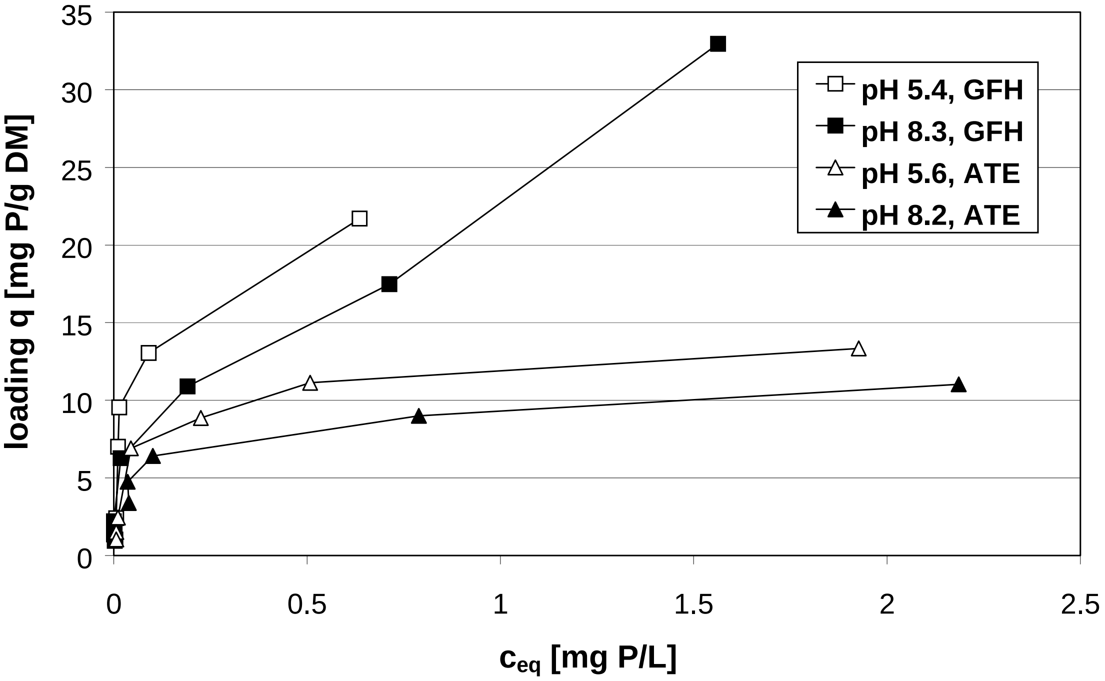

**Fig. 3.5:** Isotherms of phosphorus on GFH and ATE at different pH (± 0.2).

### 3.1.4 Influence of temperature

Because most trials were conducted at room temperature around 20 °C in the lab, the influence of lower temperature on isotherms was studied here. The used temperature of 10 °C (around the mean outside temperature in Berlin) seems to be more realistic for a future pilot- or full-scale application.

As shown in **Figure 3.6**, the temperature has no effect on P-sorption at equilibrium P-concentrations below 0.5 mg/L in the case of GFH. In contrast, the loading on ATE decreases at the lower temperature of 10 °C. Generally for sorption as an exothermic process the opposite would have been expected for ATE. The smaller P-sorption at lower temperature can also not be explained by the temperature dependency of the dissociation constant of water, because with rising temperature the dissoziation constant increases as well as the concentrations of hydrogen and hydroxyl ions. The temperature influence on P-sorption for ATE could not be explained by conducted experiments or by literature. For GFH at pH 8.3 and 20 °C, the steep increase in the isotherm might be caused by precipitation at higher equilibrium concentrations (compare **chapter 3.1.1**).

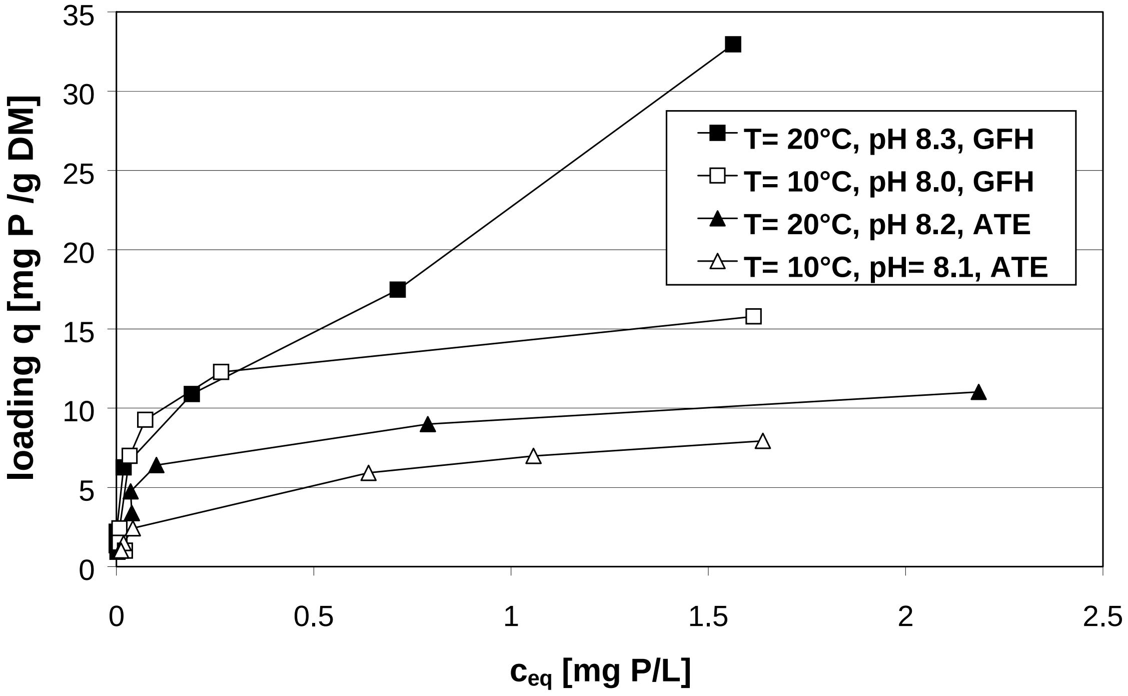

**Fig. 3.6:** Isotherms of phosphorus on GFH and ATE at 10 and 20 °C.

However, at P-concentrations < 0.5 mg/L the temperature influence is small and no improvements are expected in an outdoor application from these results.

### 3.1.5 Presence of inorganic anions

Different other inorganic anions, like chloride, sulfate, hydrogencarbonate and sometimes nitrate (compare **Tab. 2.1**), are present in MBR filtrates. In contrast to DOC, no removal of chloride, nitrate, sulfate and dissolved inorganic carbon (mostly represented by hydrogencarbonate around pH 8) could be found in dependence of sorbent mass of GFH and ATE up to 1 g.

Therefore, MBR filtrates were additionally spiked by one anion (here sulfate) to examine its influence on P-sorption. P-isotherms were determined for unspiked MBR filtrate and for spiked MBR filtrate (~ 200 - 400 mg/L). **Figure 3.7** gives P-isotherms on GFH and **Figure 3.8** on ATE in the presence of 4 to 13 times more sulfate than P on a molar basis.

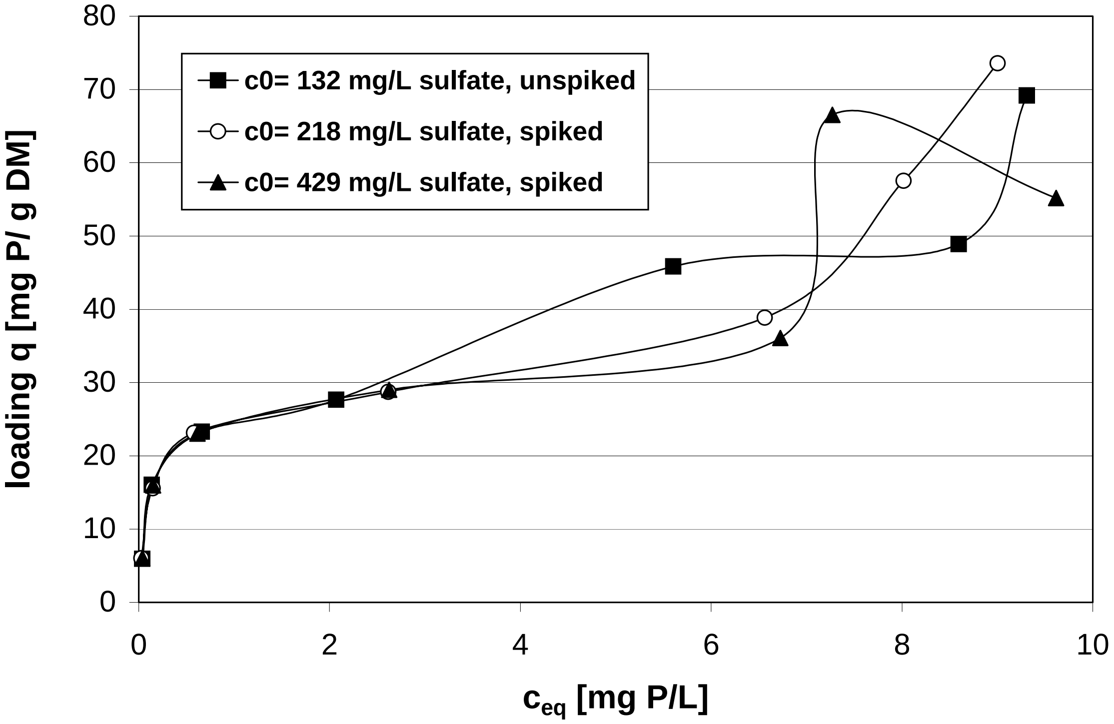

**Fig. 3.7:** P-isotherms on GFH in unspiked ($c_0$= 132 mg/L sulfate) and MBR filtrates additionally spiked with sulfate (pH 8.3).

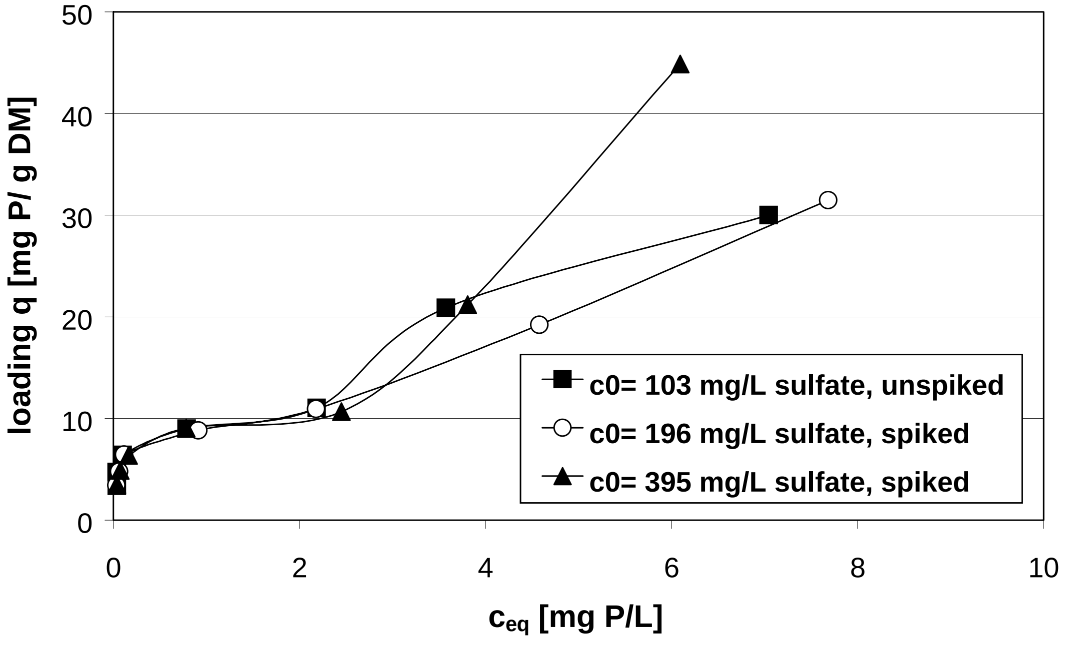

**Fig. 3.8:** P-isotherms on ATE in unspiked ($c_0$= 103 mg/L sulfate) and MBR filtrates additionally spiked with sulfate (pH 8.25).

In both cases, P-isotherms give a very similar picture without any influence by sulfate up to a relevant equilibrium P-concentration of 2 mg/L. At higher equilibrium P-concentrations, where a competition would be more recognizable, the P-isotherms are subject to fluctuations due to calculation of loading and precipitation like discussed in **chapter 3.1.1**.

A possible influence of hydrogencarbonate on P-sorption cannot be studied by spiking hydrogencarbonate due to a following pH shift. Therefore, P-sorption was investigated compared to previously decarbonated MBR filtrate (see **Figure 3.9**). Hereby, the MBR filtrate was first adjusted to pH 2 and all hydrogencarbonate/ carbonate removed as carbon dioxide by stripping with nitrogen before readjusting pH.

Again, at low equilibrium P-concentrations no differences were obtained in the presence and absence of hydrogencarbonate in P-loading. The slightly higher loading in the decarbonated MBR filtrate can be attributed to the slightly lower pH here (compare **chapter 3.1.3**).

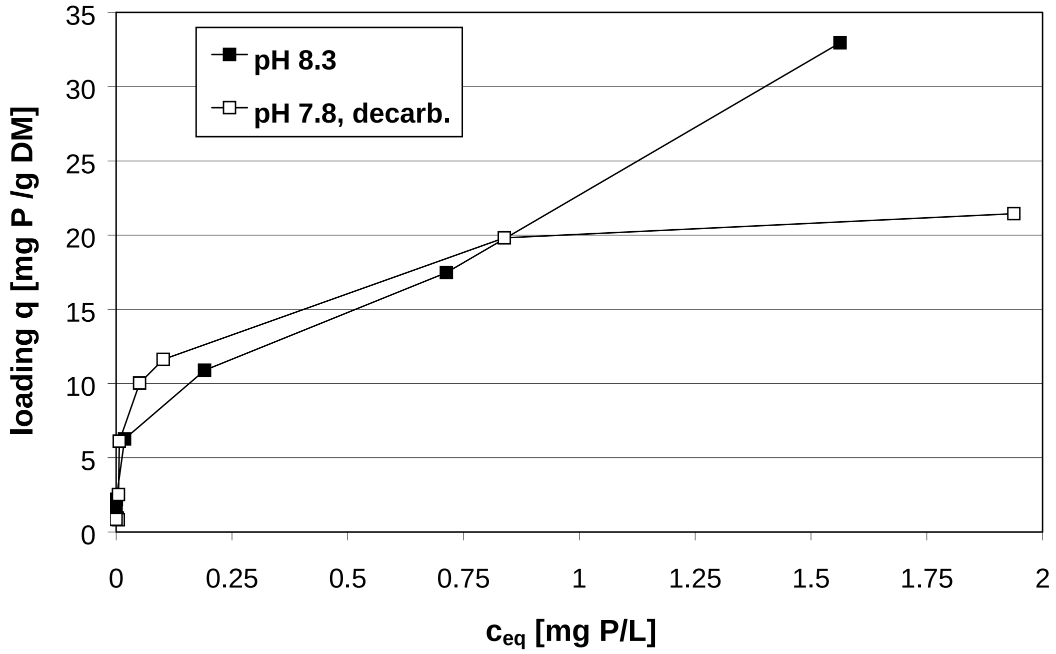

**Fig. 3.9:** P-isotherms on GFH in MBR filtrate (pH 8.3) and decarbonated MBR filtrate (pH 7.8).

The competition in anion sorption on metal hydroxide/oxide surfaces depends on their sorption mechanisms. For unspecifically sorbing anions, like chloride, nitrate and sulfate, the sorption occurs only by electrostatic forces with a positively charged sorbent surface. The isoelectric point (ieP) of pure GFH is at pH 8.2 (Teermann, 2000). For ATE no value is available, but from literature an isoelectric point is mentioned at pH 8.6 for $\gamma$-$Al_2O_3$ (Huang et al., 2001). It is known from the literature that the point of zero charge decreases strongly in the presence of phosphate and organic compounds. For goethite ($\alpha$-FeOOH) the point of zero charge can even shift to pH around 4 depending on the Fe : P-ratio (Hadeler, 1999). For the relevant pH-range it can be assumed here, that the surfaces of GFH and ATE are negatively charged in presence of MBR filtrate, which is unfavorable for unspecifically sorbing anions. For example, no sorption of sulfate could be recognized anymore above the point of zero charge for sorption on goethite ($\alpha$-FeOOH; Geelhoed et al., 1997). Additionally phosphate is known to be able to sorb specifically by ligand exchange. Therefore, the P-sorption is not hindered but reduced by negatively charged surfaces even at alkaline pH

Due to the interference in phosphate and silicate analysis, specially if silicate is spiked at low P-concentrations, the influence of silicate on P-sorption was not determined here. However, from literature it is known that silicate competition to P-sorption on iron oxides is only slightly relevant at pH below 9 (Mayer and Jarrell, 2000).

From studying the breakthrough behaviors the following sorption sequence can be stated for the investigated MBR filtrates (see **chapter 3.2**):

GEH: $PO_4^{3-} > HCO_3^{-} > SO_4^{2-} > NO_3^{-} > Cl^{-}$

ATE: $PO_4^{3-} > HCO_3^{-} \approx SO_4^{2-} > NO_3^{-} \approx Cl^{-}$.

Hereby, it has to be emphasized that the anions were not present in equimolar concentrations. The different concentrations for the anions in MBR filtrates are given in **Table 2.1**.

Summarizing, no significant competition occurred on P-sorption by other inorganic anions, which was confirmed by the breakthrough curves.

### 3.1.6 Presence of calcium

By co-sorption calcium can play an important role in sorption of anions. A negatively charged sorbent surface becomes more positive by co-sorption of calcium enabling further anion sorption. Kinetic tests with synthetic P-solution without calcium conducted in recirculating differential flow reactors showed much slower P-sorption that in tests with MBR filtrates containing calcium (not shown here). Therefore, MBR filtrates were spiked with calcium to assess if enough calcium is available in unspiked MBR filtrates for simultaneous P-sorption. MBR filtrate with a lower calcium concentration (~ 90 mg/L) than average MBR filtrates was chosen for these studies, (compare **Tab. 2.1**). **Figure 3.10** shows P-isotherms on GFH and ATE in the presence of lower and higher calcium concentrations.

No significant difference can be stated on P-isotherms in dependence on calcium concentrations of 90 and 170 mg/L, which indicates that the calcium concentration is already high enough in MBR filtrate. No further optimization can be achieved here.

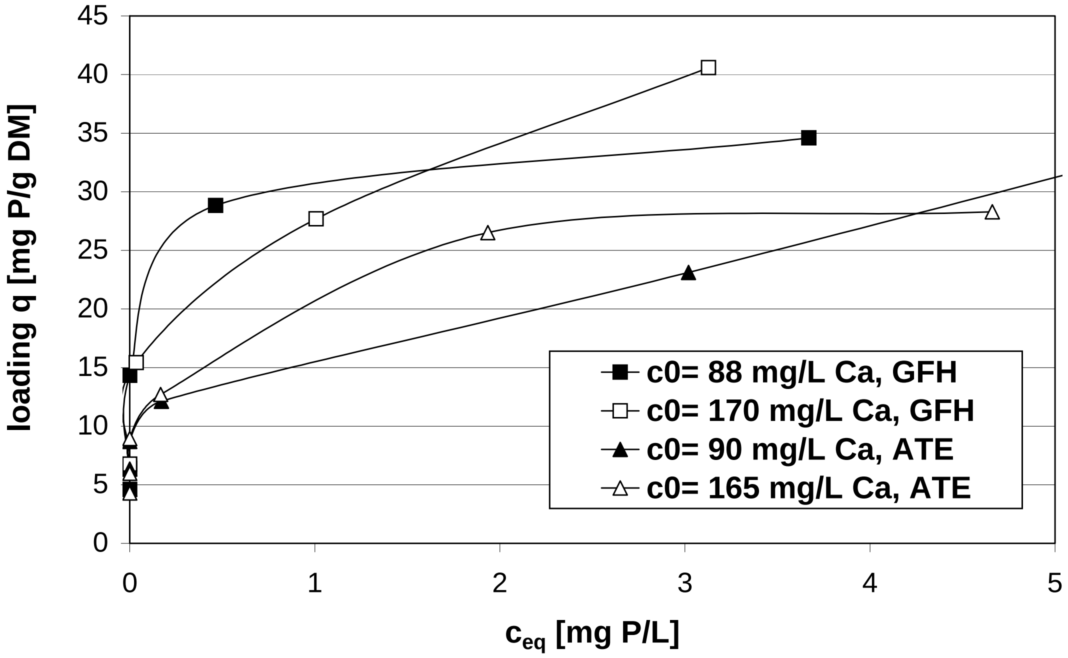

**Fig. 3.10:** P-isotherms on GFH and ATE at different initial calcium concentrations in MBR filtrates.

## 3.2 Breakthrough curves

For a first impression on the breakthrough behavior small columns were operated with a short contact time and high influent P-concentration. Subsequently, the continuous operation was optimized in larger columns with longer contact times and lower influent P-concentrations relevant in MBR filtrates.

### 3.2.1 Preliminary breakthrough behavior at high influent P-concentration

Preliminary breakthrough test were conducted in fixed-bed filters in a very small scale and at high influent P-concentrations ($c_0$= 8 mg/L P). MBR filtrates were fed continuously to test filters filled with all three sorbents. A short empty bed contact time EBCT of 10 min was used equivalent to 6 bed volumes per hour.

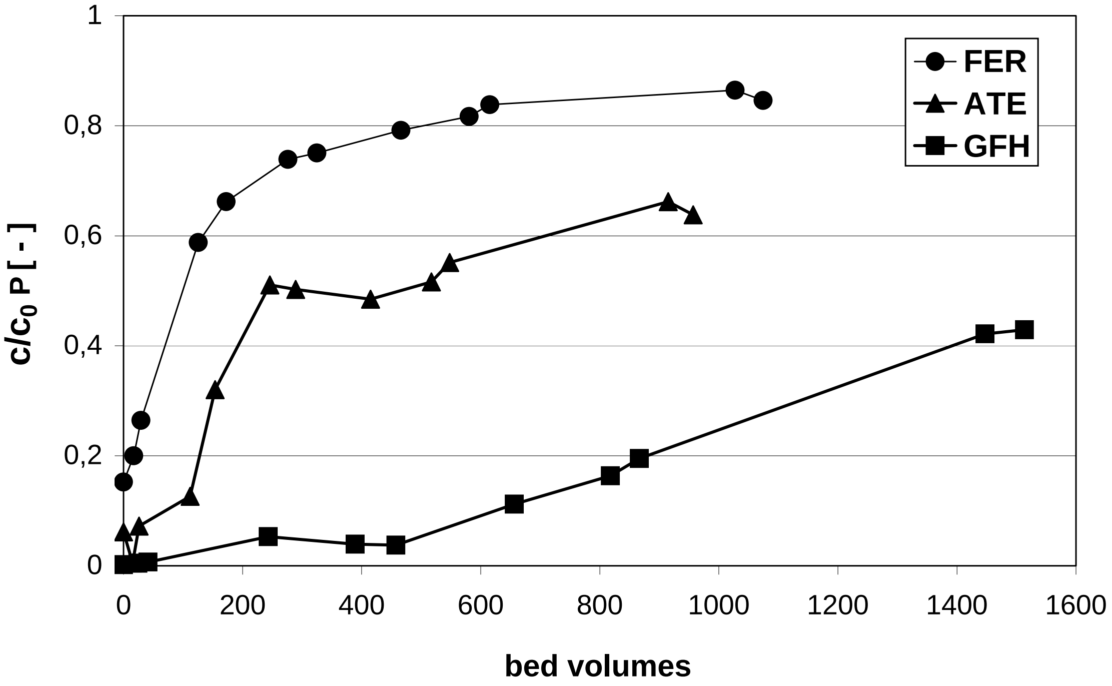

**Fig. 3.11:** Effluent P-concentration related to the influent P-concentration ($c_0$= 8 mg/L) versus bed volumes for small sorption filter in spiked MBR filtrates.

In **Figure 3.11** the effluent P-concentration normalized to each influent P-concentration is shown versus the bed volumes. Ideally a breakthrough curve should feature a zero effluent concentration for a long time resp. high bed volumes and than increase steeply. For GFH a slow increase in effluent P-concentration can be observed with a starting breakthrough at above 400 BV. In contrast, phosphorus breaks through in the effluent immediately after starting the filters for ATE and FER revealing the great influence of internal mass transfer for P-sorption here. In these two filters the contact time is too small for both sorbents (ATE and FER) to remove P completely.

For optimization the breakthrough behavior in larger columns filled with GFH and ATE was studied with samplers at different heights representing different contact times around 3 to 36 min (see **Figure 2.2**). The breakthrough of other constituents is discussed only for optimized conditions in these columns in the next chapter.

### 3.2.2 Breakthrough behavior at lower influent P-concentrations and different contact times

The larger sorption filters were operated for 14 weeks continuously without back-flushing. No clogging by particles could be observed and no pressure increase was detected, which can be explained with the low liquid volume flow rate of 2.7 mL/min used and the particle-free MBR filtrate. It is advisable to check the clogging risk in pilot scale, because of a higher liquid volume flow rate and a possible effect by microorganism growth.

MBR filtrate was spiked to 0.3 mg/L P as influent and all chemical parameters analyzed in the effluent are shown for the ATE column in **Figure 3.12** and for GFH in **Figure 3.13**. Hereby, effluent concentrations are normalized to each influent concentration. For clarity only the mean influent concentrations are given in the figure captions.

As expected from the small columns, ATE had no retaining capacity for chloride, which is the first to break through followed simultaneously by sulfate and total inorganic carbon (TIC). 60 % of the TOC was also present in the effluent immediately, which corresponds well with results from isotherms (see **Figure 3.4**), where around 6 mg/L DOC could not be sorbed by ATE. Although part of the SAC at 254 nm and 436 nm were breaking through early too, afterwards their breakthrough curves showed only a very slow increase. Finally, around 1,800 bed volumes a slow but rising breakthrough of phosphorus started, which is described in detail below.

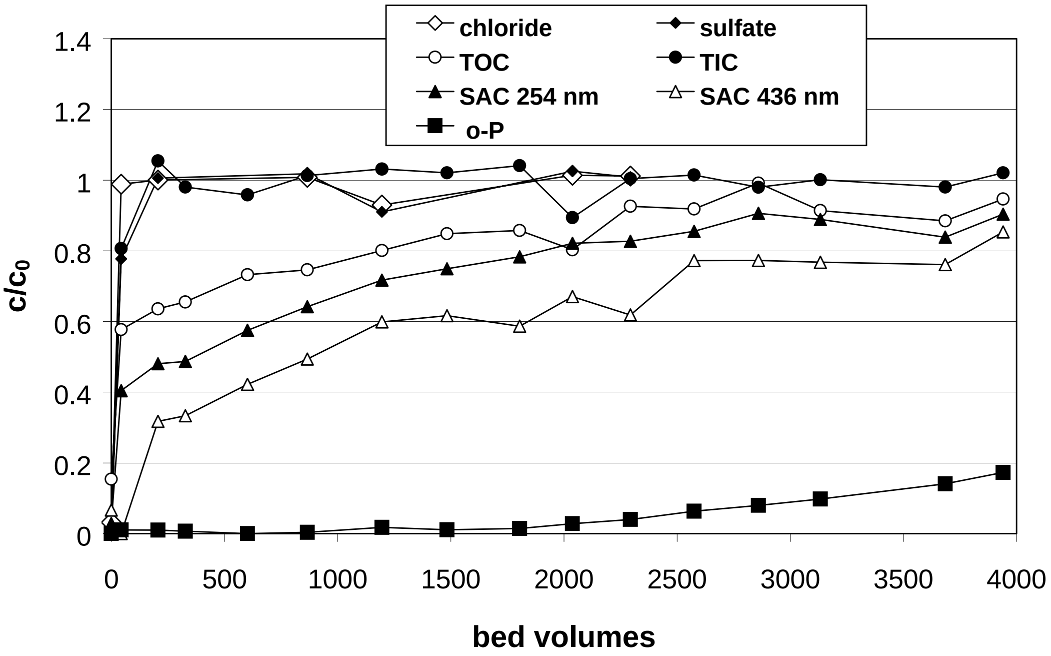

**Fig. 3.12:** Effluent concentrations related to each influent concentration (mean $c_{0.chloride}$= 193 mg/L, $c_{0.sulfate}$= 152 mg/L, $c_{0.TOC}$= 11.8 mg/L, $c_{0.TIC}$= 59 mg/L, $c_{0.SAC254nm}$= 29.1 1/m, $c_{0.SAC436nm}$= 1.64 1/m, pH 8.4) of an ATE sorption filter fed by MBR filtrate spiked to 0.3 mg/L P (EBCT= 36 min).

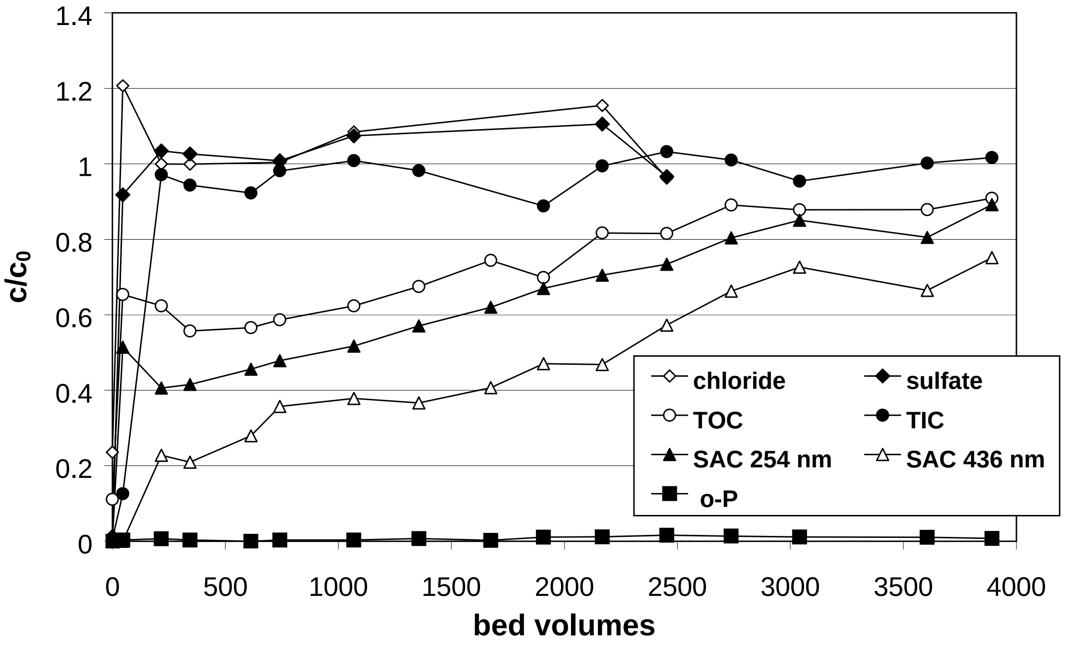

**Fig. 3.13:** Effluent concentrations related to each influent concentration (mean $c_{0.chloride}$= 193 mg/L, $c_{0.sulfate}$= 152 mg/L, $c_{0.TOC}$= 11.8 mg/L, $c_{0.TIC}$= 59 mg/L, $c_{0.SAC254nm}$= 29.1 1/m, $c_{0.SAC436nm}$= 1.64 1/m, $c_{0.o\text{-}P}$= 0.3 mg/L, pH 8.4) of a GFH sorption filter fed by MBR filtrate spiked to 0.3 mg/L P (EBCT= 36 min).

In the column filled with GFH, an increase was monitored for chloride above its influent concentration. This is caused by desorption of chloride, which remains in the structure of GFH during production process from ferric chloride. In contrast to ATE, sulfate broke through before TIC. Compared to ATE, GFH showed a better performance in removing organics as expected from isotherms (**chapter 3.1.2**). Particularly the better retention of phosphorus by GFH is striking (**Figure 3.13**).

Samplers over column height represent different bed volumes and empty bed contact times EBCT. **Figure 3.14** reveals that the contact time had a great influence on P-sorption by ATE, which is caused by the internal mass transfer discussed in **chapter 3.2.1**. The limit of 50 µg/L P in the effluent was reached at 4,000 bed volumes at the longest EBCT of 36 min. However, EBCT of 33.6 min gives nearly the same result indicating that 30 min EBCT should be considered as cost-effective operation parameter.

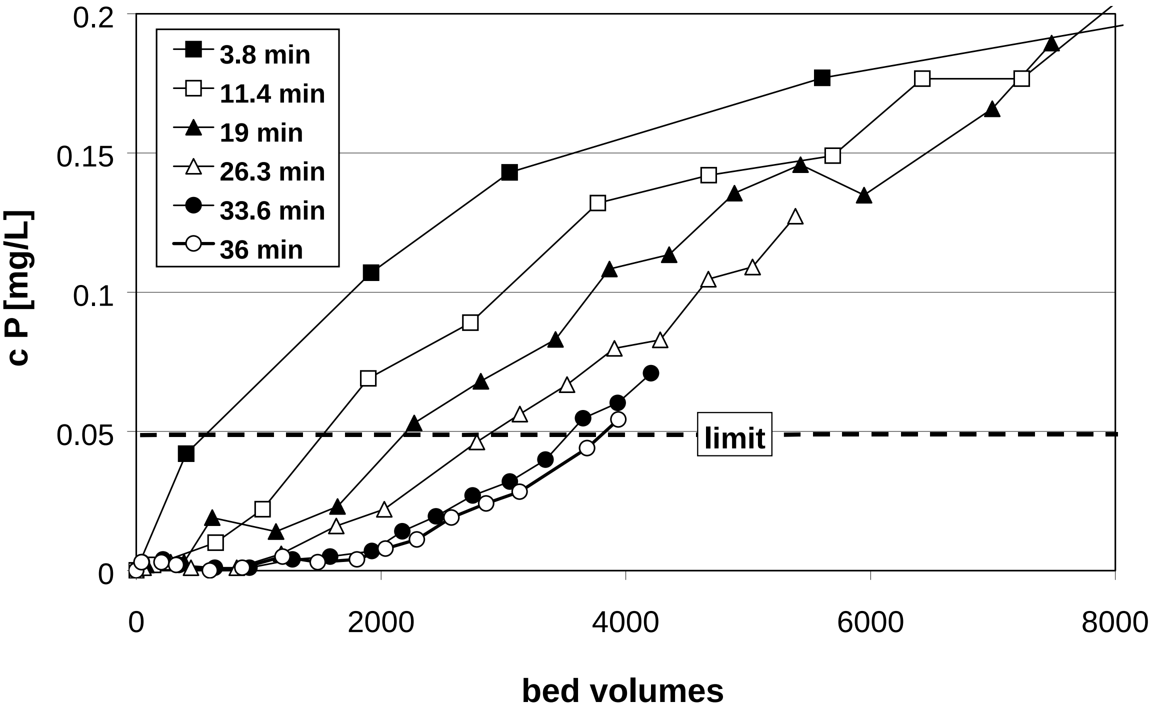

**Fig. 3.14:** Effluent P-concentrations at different contact times versus bed volumes of an ATE sorption filter fed by MBR filtrate spiked to $c_0$= 0.3 mg/L P.

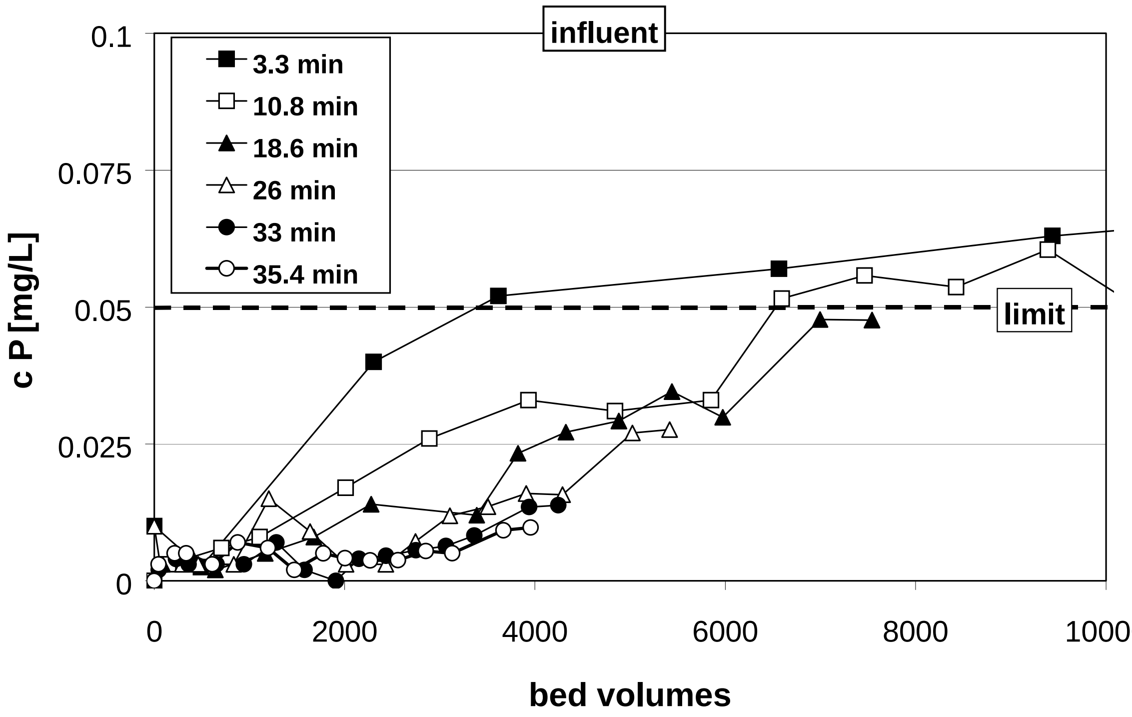

**Fig. 3.15:** Effluent P-concentrations at different contact times versus bed volumes of an ATE sorption filter fed by MBR filtrate spiked to $c_0$= 0.1 mg/L P.

At the lower influent concentration of 0.1 mg/L P, the operation time of 14 weeks was not long enough to reach a breakthrough at contact times above 18.6 minutes. At EBCT of 18.6 min the limit of 50 µg/L P was reached after 8,000 bed volumes (**Figure 3.15**). However, its is expected that even more bed volumes can be put through the ATE filter at EBCT ≥ 26 min.

At both influent P-concentrations the GFH-columns proved a better performance. At the influent concentration of 0.3 mg/L P a breakthrough at 8,000 bed volumes was observed, while at the influent concentration of 0.1 mg/L P the limit of 50 µg/L P was not reached at any contact time up to then (**Figures 3.16** and **3.17**). Due to the better retention by GFH less breakthroughs could be detected at the different contact times compared to ATE. Furthermore, no clear dependence could be found between longer contact time and a higher throughput of bed volumes. At the lower influent concentration of 0.1 mg/L P, the fluctuations by P-analyses in the low effluent P-concentrations are too high for stating any differences (**Figure 3.17**). While at the influent concentration of 0.3 mg/L P (**Figure 3.16**) the bed volume decreases from 9,000 at 2.4 min to 8,000 at 10 min EBCT. This is probably effected by a classification of GFH during backwashing before loading. Consequently, finer particles could be found at the top of the column with a higher sorption capacity for P-removal leading to higher bed volumes throughput. The influence of backwashing, which is recommended by the manufacturer for removing air in the bed after filling, seems to be too strong for this small column dimension in connection with the wide particle distribution. As a side effect, the tendency of GFH for abrasion is revealed.

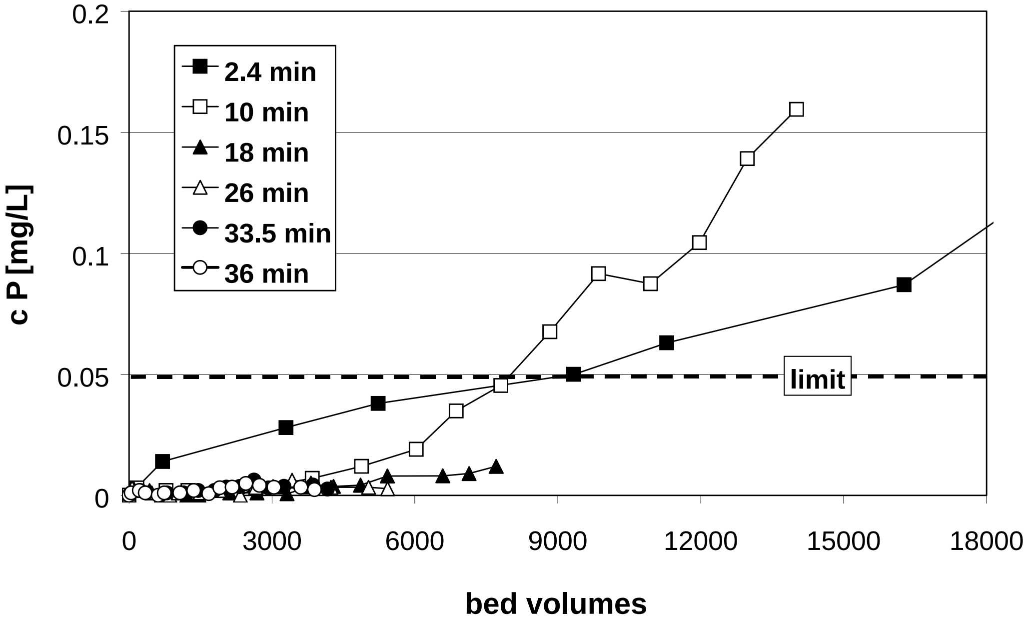

**Fig. 3.16:** Effluent P-concentrations at different contact times versus bed volumes of a GFH sorption filter fed by MBR filtrates spiked to $c_0$= 0.3 mg/L P.

In the determination of isotherms (**chapter 3.1**) no differences were found in the removal of ortho- and total-phosphorus due to the low particulated phosphorus content. In columns an additional removal of particles by a filter effect might be possible. However, the removal of ortho- and total-phosphorus is very similar in columns likewise, which is shown in **Figure 3.18** for GFH and ATE at different contact times EBCT each fed by MBR filtrates spiked to 0.3 mg/L P.

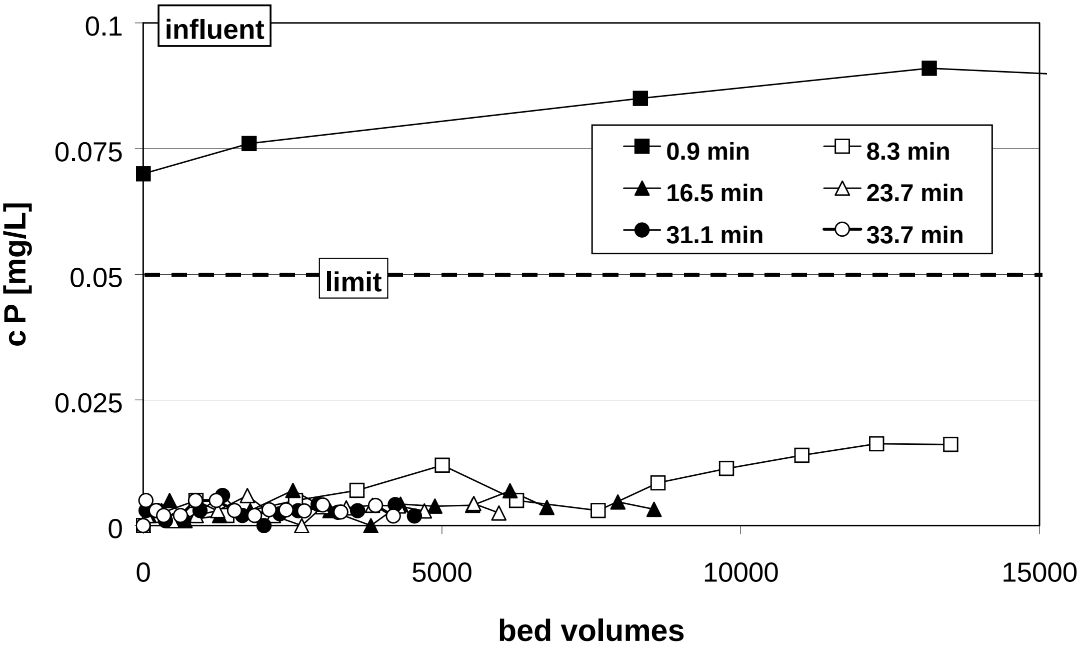

**Fig. 3.17:** Effluent P-concentrations at different contact times versus bed volumes of a GFH sorption filter fed by MBR filtrate spiked to $c_0$= 0.1 mg/L P.

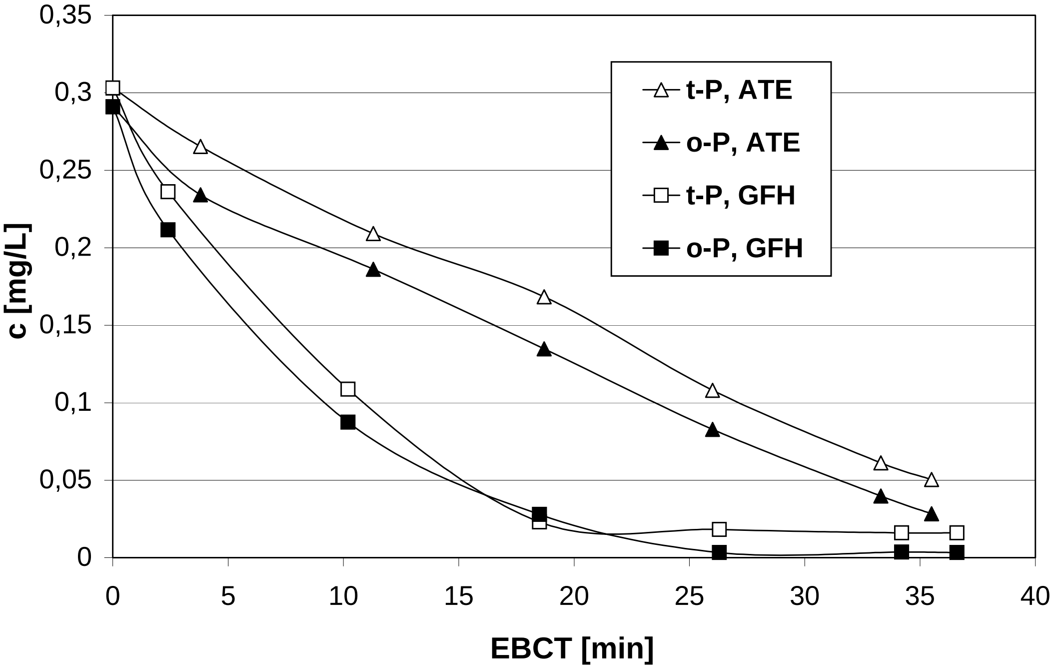

**Fig. 3.18:** Effluent ortho- and total-P-concentrations versus different contact times EBCT of a GFH and ATE sorption filter fed by MBR filtrates spiked to $c_0$= 0.3 mg/L P.

Overall, GFH shows a better performance in removing P and organics in sorption filters than ATE, which was already foreseen by batch experiments.

## 3.3 Regeneration

Regeneration of loaded sorbent is a precondition for its reuse reducing sorbents costs and therefore capital cost. Sodium hydroxide is known as a suitable regenerate for metal hydroxides/oxides. Due to the long operation time a regeneration and reloading could not be examined in sorption filters. Therefore, regeneration was studied in differential recirculating flow reactors with a small mass of sorbent (m= 0.25 g DM).

In general, regeneration success can be judged by extraction efficiency giving the amount of P desorbed from loaded sorbents and by the regained adsorption capacity after regeneration.

An extraction efficiency of 58 % was achieved and reproduced using 0.6 M NaOH for GFH previously loaded with spiked MBR filtrate. Hereby, the extraction efficiency showed no dependence on the regeneration time between 16 and 72 h. Therefore, it should be investigated if the regeneration time might still be shorter. For ATE an extraction efficiency could not be determined, because $AlOH_3$ and probably $AlPO_4$ precipitated and interfered during neutralization of regenerate for analyses. This is caused by a partly dissolving of aluminum from ATE in the presence of sodium hydroxide. This dissolution of activated alumina by sodium hydroxide is also known from the literature. Therefore, the regeneration can not be judged by the extraction efficiency in the case of ATE.

To assess reloading fresh layers of ATE and GFH were loaded in differential recirculating flow reactors by spiked MBR filtrate first, regenerated by 0.6 and 2.8 M NaOH or 3 % $H_2O_2$, rinsed with water afterwards for adjustment to neutral pH and than reloaded again under the same conditions. For determination of still existing sorption capacity additional control columns were reloaded without regeneration. **Figure 3.19** gives the first loading of phosphorus on fresh sorbents (load 1) compared to three reloadings (load 2 - 4).

The control columns, which were not regenerated before reloading, reveal that still adsorption capacity exists for P (**Figure 3.19**) and SAC 254 nm (**Figure 3.20**). For reloading of P the regeneration of GFH by 0.6 M NaOH seems most effective, while the oxidative regeneration by 3 % $H_2O_2$ gives the highest reloading in SAC. Hereby, hydrogen peroxide is activated by ferric hydroxide to OH-radicals initiating the unspecific oxidation of sorbed organics on GFH. The aim is to regain sorption capacity for P by desorption of formed smaller organic oxidation products. The better reloading of SAC compared to P indicates that both constituents are sorbed at different sites, which might be explained by their different sizes. The oxidative regeneration of GFH was optimized for textile wastewater treatment (Kornmüller et al., 2000, 2001) featuring very different conditions compared to MBR filtrates. Therefore, more detailed experiments would be necessary to judge the long-term success of oxidative regeneration.

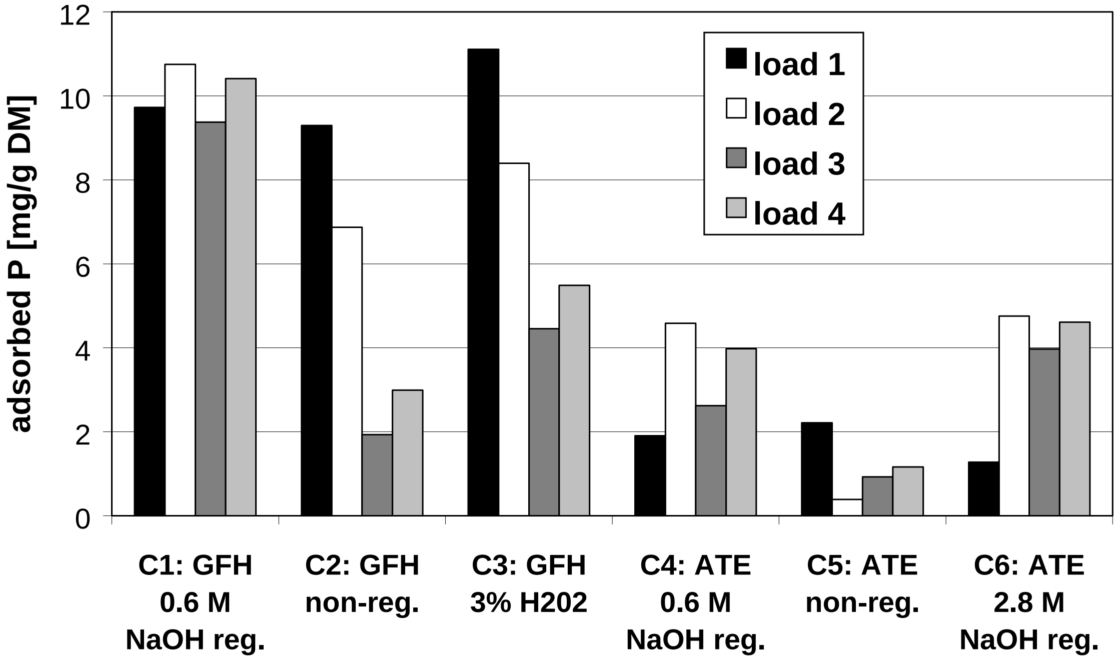

**Fig. 3.19:** First loading of P on fresh sorbents (load 1) compared to reloading (load 2 - 4, 68 h, pH 8.2 ±0.2 , MBR filtrates spiked to $c_0$= 4 mg/L P) of GFH and ATE layers, which were non-regenerated or regenerated by 0.6 or 2.8 M NaOH or 3% $H_2O_2$ in differential recirculating flow reactors (reg. 1: 17 h, reg. 2: 16 h, reg. 3: 68 h).

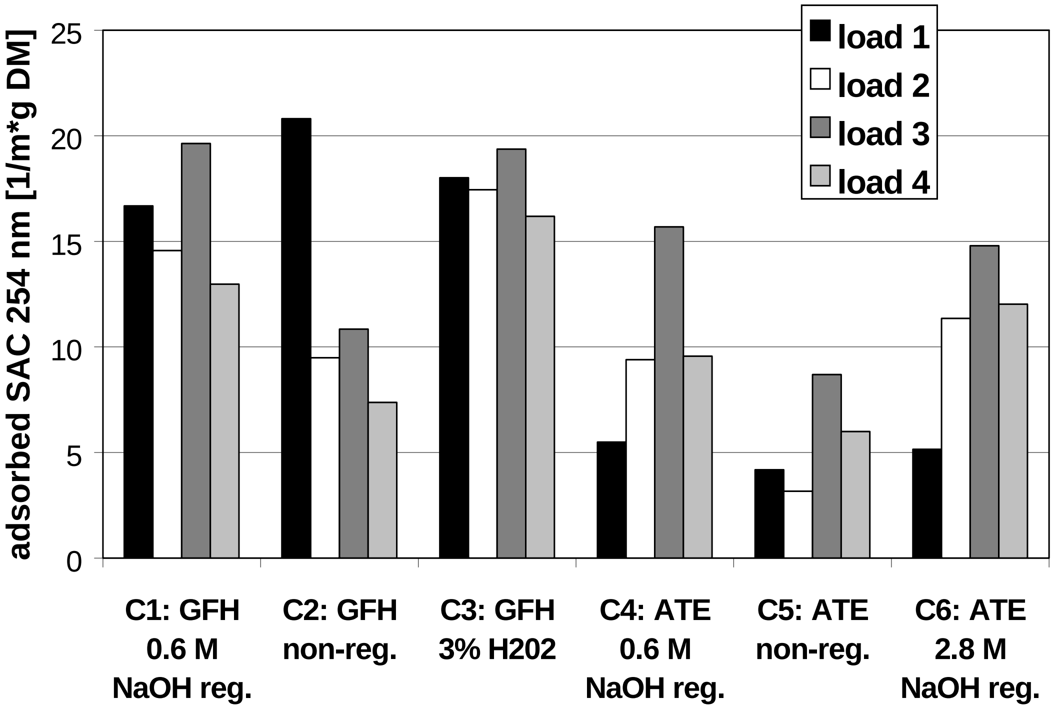

**Fig. 3.20:** First loading of SAC 254 nm on fresh sorbents (load 1) compared to reloading (load 2 - 4, 68 h, pH 8.2 ±0.2) of GFH and ATE layers, which were non-regenerated or regenerated by 0.6 or 2.8 M NaOH or 3% $H_2O_2$ in differential recirculating flow reactors (reg. 1: 17 h, reg. 2: 16 h, reg. 3: 68 h).

Concerning reloading of ATE, first it has to be mentioned that the first loading is too low. Normally half the loading of GFH is obtained using ATE (compare **chapter 3.1.1**). Therefore a loading around 5 mg P per mg DM ATE was expected. A reason for the low value in all first ATE loadings could not be stated (the pH stayed stable around 8.2). For ATE the regeneration by NaOH is possible for P- and SAC-reloading. However, the gain in loading by the higher concentrated NaOH was small. Due to the increasing dissolution of aluminum, 2.8 M NaOH is the highest concentration recommended (Hildebrandt, 2000). In continuous regeneration of coarsed activated alumina in fixed bed filters by Donnert (1988), a redissolution of phosphorus of 71 % could be obtained by using 0.5 M NaOH for 7 hours. Hereby, the NaOH concentration was continuously readjusted including a lime precipitation step every hour. The loss in activated alumina was 2 %.

Although a partial reloading of ATE and GFH could be achieved by NaOH-regeneration compared to control columns, these results can not be easily transferred from the application in differential recirculating flow reactors to larger sorption filters for different reasons:

- Due to the low sorbent mass used in the differential recirculating flow reactor the consumption of NaOH was very low. By titration a NaOH-consumption of 1 % were determined after regeneration of GFH and 3 % by ATE. A much higher consumption of NaOH is expected in larger scale filters. Therefore, no prediction is possible about the NaOH lost and the reuse of NaOH.
- Normally 2 - 4 bed volumes of regenerate is used in sorption filters. Because of the small sorbent layer in differential recirculating flow reactors, the volume ratio of NaOH to the bed volume was 100 : 1, so that these results were obtained under very optimized conditions.
- Here the sorbents were only loaded for 68 h and the maximum loading was not achieved yet. In sorption filters with an operation time over weeks phosphorus might be sorbed very tightly and deep inside particles giving a non-extractable P amount. From competition experiments on goethite ($\alpha$-FeOOH) a nonexchangeable P-fraction is known with a mean value of 34 % up to relatively short sorption times of 288 h (Hongshao and Stanforth, 2001). Therefore, the quantities of reloading and the effect of mechanical stress applied on sorbents due to backwashing and regeneration can not be estimated from these experiments.

For these reasons, intensified regeneration experiments are recommended in sorption filters of pilot scale. Influencing parameter should be studied in sorption filters like the dependency of sorption time on regeneration time, the regeneration time, the concentration of regenerate and the number of reloadings before disposal of sorbent.

# 4 Cost Estimation

### Investment Costs

A first estimation of investment costs for GFH-adsorption was performed using data from a former project targeted on removal of arsenic from groundwater in Stadt Oldendorf, Germany (Seith and Jekel, 1999). A balance period of 10 years was chosen concerning depreciation and credit term. Furthermore, linear depreciation over 10 years and linear credit paying-offs (interest rate 7 % p.a.) were used for calculation. Investment costs for ATE adsorption were assumed to be 3.5 times higher than for GFH adsorption due to the 3.5 times larger filter area needed to reach 30 min empty bed contact time.

The costs for the regeneration technique were roughly estimated against the background of a more expensive handling of the chemicals NaOH and $H_2SO_4$. It is assumed that 0.6 M NaOH and 0.3 M $H_2SO_4$ are produced on-site by dosing of concentrates into the piping. The neutralized regenerate is stored in a tank and is slowly and continuously discharged into the influent of the MBR. Because of the buffer strength in MBR a neutralization might not be necessary which would lower the costs here. Four bed volumes NaOH (24 $m^3$ resp. 84 $m^3$) are used for regeneration. A potential conditioning step and the loss of GFH (ATE) during backwashing and regeneration were neglected. Regarding regeneration, only one-way use of NaOH was assumed. The disposal costs for ATE were neglected.

### Operating costs

Operating costs were estimated using current market prices (GFH, ATE, NaOH, $H_2SO_4$, tap water). Maintenance was assumed to require 0.5 h working hours every day. Energy costs were flat valued with 1 Cent per $m^3$ treated water for both sorbents.

### Scenarios a, b and c

For better comparison, three scenarios (a, b, c) were calculated on a 10-year basis for each sorbent. Scenarios a and b are based on the assumption that the capacity for P removal is the same before and after regeneration, i.e. 100 % reloading can be achieved by regeneration - a and b differ only in the period GFH (resp. ATE) can be used until disposal. Since no long-term experiences are available regarding regeneration of GFH and ATE, scenario a acts on the assumption that after 100,000 BV for GFH (50,000 BV for ATE) replacement of the material becomes necessary. Scenario b emanates from 300,000 BV (150,000 BV for ATE).

For scenario c it is assumed that only 50 % of the initial capacity is regained after each regeneration, respectively. I.e., after the second regeneration only 25 % of the initial capacity would be available, etc. In this particular case, a rather quick replacement of GFH (ATE) would be necessary to obtain reasonable operation times between regeneration intervals. Therefore, a discharge is assumed after every two regenerations (26,250 BV for GFH). An additional regeneration would only lengthen the operation time e.g. for GFH to 28,125 BV. Consequently, very high operating costs are expected in this worst-case scenario.

Generally, estimations were based upon the following operational parameters:

| **parameter** | **assumption** |
|---|---|
| amount of treated water | 1000 $m^3$/d (42 $m^3$/h) |
| total throughput in 10 years | 3,600,000 $m^3$ |
| influent P-concentration | 100 µg/L |
| effluent P-concentration | < 50 µg/L P |

Regarding regeneration costs, an additional calculation was performed for an influent P concentration of 0.3 mg/L, respectively.

| **GFH** | | **ATE** | |
|---|---|---|---|
| adsorber volume | 6 $m^3$ | adsorber volume | 21 $m^3$ |
| empty bed contact time | 8.6 min<br>(7 BV/h) | empty bed contact time | 30 min<br>(2 BV/h) |
| capacity for P-removal | 15,000 bed volumes (complies with 90 d) | capacity for P-removal | 8,000 bed volumes (complies with 166 d) |
| total throughput in 10 years | 600,000 BV | total throughput in 10 years | 171,000 BV |

## Investment costs for GFH

### GFH-Adsorption

| | |
|---|---|
| filter vessel (6 $m^3$) | 25,000 € |
| pump incl. electronic control equipment | 30,000 € |
| equipment for backwashing | 2,000 € |
| Total | 57,000 € |

| | |
|---|---|
| costs per year: | 5,700 € |
| rates per year (7 % p.a.) | 1,995 € |
| **total costs per year:** | **7,695 €** |

### Regeneration

| | |
|---|---|
| tank for neutralized regenerate (30 $m^3$) | 20,000 € |
| 2 dosage pumps | 5,000 € |
| piping, static mixers, miscellaneous | 15,000 € |
| chemicals building | 40,000 € |
| Total | 80,000 € |

| | |
|---|---|
| costs per year: | 8,000 € |
| rates per year (7 % p.a.) | 2,800 € |
| **total costs per year:** | **10,800 €** |

## Operating costs for GFH

### Sorbent GFH

| | |
|---|---|
| GFH, price per ton | 4,200 € |
| GFH, price per $m^3$ (density 1250 kg/$m^3$) | 5,250 € |
| (including disposal of GFH and backwash sludge) | |
| **costs per charge GFH (6 $m^3$)** | **31,500 €** |

### Regeneration

| | |
|---|---|
| NaOH (33 %, ≈10 M), price per ton 400 € | |
| dilution to 0.6 M (≈ 1:16), 1.5 $m^3$ | |
| costs per regeneration (24 $m^3$ 0.6 M NaOH) | 600 € |
| neutralization with $H_2SO_4$ | |
| $H_2SO_4$ (96 %, ≈10 M), price per ton 120 € | |
| dilution to 0.3 M (≈ 1:33), 0.75 $m^3$ | |
| costs per regeneration (24 $m^3$ 0.3 M $H_2SO_4$) | 90 € |
| water costs (24 $m^3$ tap water) | 93 € |
| **costs per regeneration (NaOH, $H_2SO_4$, water)** | **783 €** |

### Backwashing

| | |
|---|---|
| **water costs per backwash (20 $m^3$)** | **80 €** |

### Maintenance costs

| | |
|---|---|
| **0,5 h per day** | **15 €** |

### Energy costs

| | |
|---|---|
| **costs per $m^3$ treated water** | **0.03 €** |

## Investment costs for ATE

### ATE-Adsorption

| | | |
|---|---|---|
| filter vessel (21 $m^3$) | | 90,000 € |
| pump incl. electronic control equipment | | 40,000 € |
| equipment for backwashing | | 8,000 € |
| | Total | 138,000 € |
| | costs per year: | 13,800 € |
| | rates per year (7 % p.a.) | 4,830 € |
| | **total costs per year:** | **18,630 €** |

### Regeneration

| | | |
|---|---|---|
| tank for neutralized regenerate (90 $m^3$) | | 50,000 € |
| 2 dosage pumps | | 5,000 € |
| piping, static mixers, miscellaneous | | 15,000 € |
| chemicals building | | 40,000 € |
| | Total | 110,000 € |
| | costs per year: | 11,000 € |
| | rates per year (7 % p.a.) | 3,850 € |
| | **total costs per year:** | **14,850 €** |

## Operating costs for ATE

### Sorbent ATE

| | |
|---|---|
| ATE, price per ton | 1,200 € |
| ATE, price per $m^3$ (density 900 $kg/m^3$) | 1,080 € |
| **costs per charge ATE (21 $m^3$)** | **22,680 €** |

### Regeneration

| | |
|---|---|
| NaOH (33 %, ≈10 M), price per ton 400 € | |
| dilution to 0,6 M (≈ 1:16), 5.2 $m^3$ | |
| costs per regeneration (84 $m^3$ 0.6 M NaOH) | 2,100 € |
| neutralization with $H_2SO_4$ | |
| $H_2SO_4$ (96 %, ≈10 M), price per ton 120 € | |
| dilution to 0.3 M (≈ 1:33), 2.5 $m^3$ | |
| costs per regeneration (84 $m^3$ 0.3 M $H_2SO_4$) | 305 € |
| water costs (84 $m^3$ tap water) | 326 € |
| **costs per regeneration (NaOH, $H_2SO_4$, water)** | **2,731 €** |

### Backwashing

| | |
|---|---|
| **water costs per backwash (80 $m^3$)** | **320 €** |

### Maintenance costs

| | |
|---|---|
| **0,5h per day** | **15 €** |

### Energy costs

| | |
|---|---|
| **costs per $m^3$ treated water** | **0.01 €** |

## GFH: Scenario 1a and 1b

Assumptions:

- regeneration after every 15,000 bed volumes throughput
- the complete capacity is regained after regeneration (100% reloading)
- GFH disposal and substitution after 100,000 (1a) or 300,000 (1b) bed volumes

Investment costs p. a. :

| | |
|---|---|
| Adsorption technique | 7,695 € |
| Regeneration technique | 10,800 € |
| **Total costs p.a.** | **18,495 €** |

GFH costs p.a. :

| Scenario | Throughput until replacement | charges replaced in 10 years | total costs in 10 years | costs p.a. | interest rates p.a. | total costs p.a. |
|---|---|---|---|---|---|---|
| 1 (a) | 100,000 BV | 6x | 189,000 € | 18,975 € | 1,103** | **20,078 €** |
| 1 (b) | 300,000 BV | 2x | 63,000 € | 6,300 € | 1,103 * | **7,400 €** |

* assumed depreciation period = 5 a ** assumed depreciation period = 1.66 a

Costs for regenerations p.a. :

| | |
|---|---|
| 40 regenerations in 10 years (783 € each) | 31,320 € |
| Total costs p.a. | **3,132 €** |

Costs for regenerations p.a. for an influent concentration of 0.3 mg/L P :

| | |
|---|---|
| 75 regenerations in 10 years (783 € each) | 58,725 € |
| Total costs p.a. | **5,873 €** |

Costs for backwash water p.a. :

| | |
|---|---|
| backwash every 4 weeks (every 5,040 BV) | |
| ⇒ 120 x in 10 years (80 € each) | 9,600 € |
| costs p.a. | **960 €** |

Maintenance costs p.a. :

| | |
|---|---|
| 912 h maintenance in 10 years (30 € each) | 54,750 € |
| costs p.a. | **5,475 €** |

Energy costs p.a. :

| | |
|---|---|
| 3,600,000 $m^3$ in 10 years (0.01 € each) | 36,000 € |
| costs p.a. | **3,600 €** |

**GFH: Scenario 1c**

Assumptions:

- only 50 % reloading capacity after regeneration
- disposal and substitution of GFH after 2 regenerations
- regeneration after every 15,000 and 7,500 BV throughput, respectively

GFH costs p.a. :

| Scenario | Throughput until replacement | charges replaced in 10 years | total costs in 10 years | costs p.a. | interest rates p.a. | total costs p.a. |
|---|---|---|---|---|---|---|
| 2 | 26,250 BV | 23x | 724,500 € | 72,450 € | - | **72,450 €** |

Regeneration costs p.a. :

1. regeneration after 15,000 BV
2. regeneration after another 7,500 BV
3. disposal and substitute of GFH after another 3,750 BV

⇒ in average regeneration every 13,125 BV

| | |
|---|---|
| 46 regenerations in 10 years (783 € each) | 36,018 € |
| costs p.a. | **3,601 €** |

Regeneration costs p.a. for an influent P concentration of 0.3 mg/L:

1. regeneration after 8,000 BV
2. regeneration after another 4,000 BV
3. disposal and substitute of GFH after another 2,000 BV

⇒ in average regeneration every 7000 BV

| | |
|---|---|
| 86 regenerations in 10 years (783 € each) | 67,338 € |
| costs p.a. | **6,734 €** |

Maintenance and energy costs remain the same as in 1a) and 1b).

## ATE: Scenario 2a and 2b

Assumptions:

- regeneration after every 8,000 bed volumes throughput
- the complete capacity is regained after regeneration (100 % reloading)
- ATE disposal and substitution after 50,000 (1a) or 150,000 (1b) bed volumes

Investment costs p. a. :

| | |
|---|---|
| Adsorption technique | 18,630 € |
| Regeneration technique | 14,850 € |
| **Total costs p.a.** | **33,480 €** |

ATE costs p.a. :

| Scenario | Throughput until replacement | charges replaced in 10 years | total costs in 10 years | costs p.a. | interest rates p.a. | total costs p.a. |
|---|---|---|---|---|---|---|
| 2 (a) | 50,000 BV | 3.4x | 77,112 € | 7,711 € | 793 € | **8504 €** |
| 2 (b) | 150,000 BV | 1,14x | 25,855 | 2,586 € | 793 € | **3378 €** |

* assumed depreciation period = 8.7 a ** assumed depreciation period = 2.9 a

Costs for regenerations p.a. :

| | |
|---|---|
| 21 regenerations in 10 years (2731 € each) | 57,351 € |
| Total costs p.a. | **5,735 €** |

Costs for regenerations p.a. for an influent P concentration of 0.3 mg/L:

| | |
|---|---|
| 43 regenerations in 10 years (2731 € each) | 117,433 € |
| Total costs p.a. | **11,743 €** |

Costs for backwash water p.a. :

| | |
|---|---|
| backwash every 4 weeks (every 1340 BV) | |
| ⇒ 120 x in 10 years (80 € each) | 9,600 € |
| costs p.a. | **960 €** |

Maintenance costs p.a. :

| | |
|---|---|
| 912 h maintenance in 10 years (30 € each) | 54,750 € |
| costs p.a. | **5,475 €** |

Energy costs p.a. :

| | |
|---|---|
| 3,600,000 $m^3$ in 10 years (0.01 € each) | 36,000 € |
| costs p.a. | **3,600 €** |

**ATE: Scenario 2c**

Assumptions:

- only 50 % reloading capacity after regeneration
- disposal and substitution of ATE after 2 regenerations
- regeneration after every 8,000 and 4,000 bed volumes throughput

ATE costs p.a. :

| **Scenario** | **Troughput** | **charges replaced in 10 years** | **total costs** | **costs p.a.** | **interest rates p.a.** | **total costs p.a.** |
|---|---|---|---|---|---|---|
| 2c | 14,000 BV | 12x | 272,160 € | 27,216 € | | **27,216 €** |

Regeneration costs p.a. :

1. regeneration after 8,000 BV
2. regeneration after another 4,000 BV
3. disposal and substitute of ATE after another 2,000 BV

⇒ in average regeneration every 7,000 BV

| | |
|---|---|
| 25 regenerations in 10 years (2,731 € each) | 68,275 € |
| costs p.a. | **6,827 €** |

Regeneration costs p.a. for an influent concentration of 0.3 mg/L P

1. regeneration after 4,000 BV
2. regeneration after another 2,000 BV
3. disposal and substitute of ATE after another 1,000 BV

⇒ in average regeneration every 3,500 BV

| | |
|---|---|
| 49 regenerations in 10 years (2,731 € each) | 133,819 € |
| costs p.a. | **13,382 €** |

## Comparison of Scenarios

The calculated cost distribution for GFH is shown in **Figure 4.1.** In general, costs for regeneration, energy, maintenance and backwashing are small in view of the high investment costs and costs for GFH.

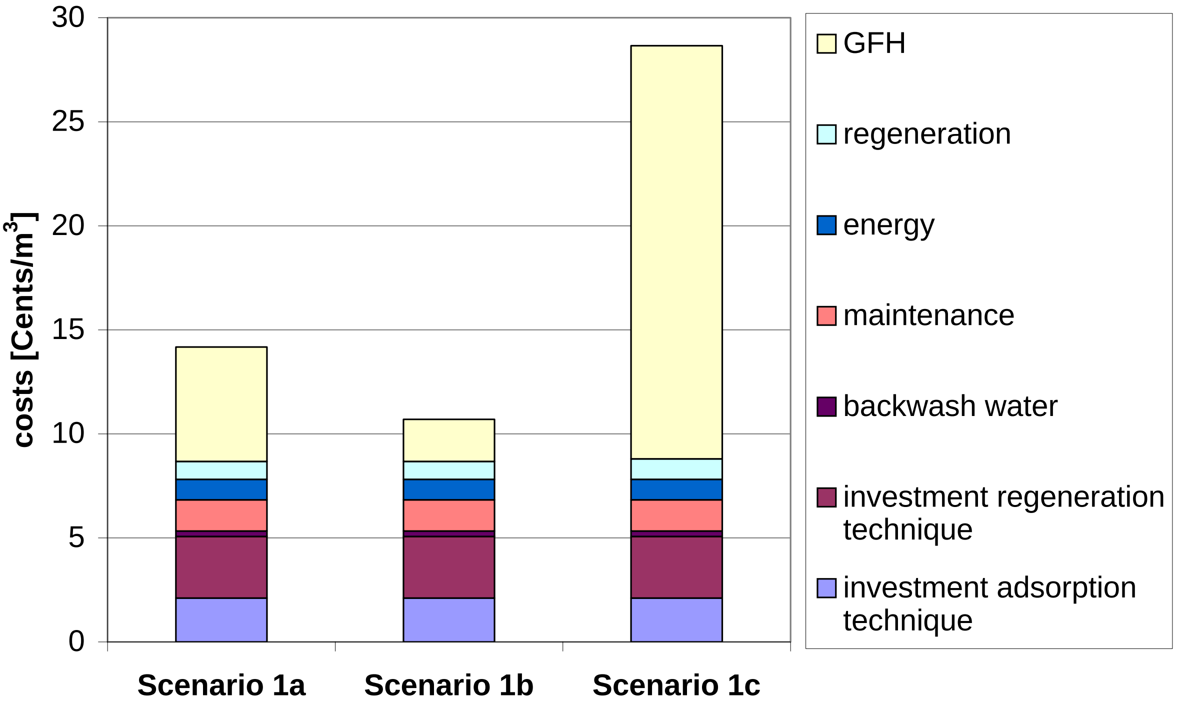

**Fig. 4.1:** Costs in Cents per $m^3$ treated water for GFH-adsorption (10 years of operation) for Scenarios 1a, 1b, 1c.

In scenario 1a, investment costs equal roughly the costs for GFH. In contrast, in scenario 1b the investment costs are the determinative expense factor. However, scenario 1b seems not to be realistic in view of the experiences made with the stability of GFH. It has to be considered that the hydraulic stress applied to the material is large during backwashing and regeneration. In view of the relative high GFH costs, loss of material and loss in reloading capacity would have an extreme cost effect. With this background, scenario 1a seems to be more realistic than scenario 1b. The mentioned extreme effect of lower capacity on the costs can be observed in scenario 1c. Due to the frequent substitution of GFH, the costs are heavily dominated by GFH (ca. 70 %).

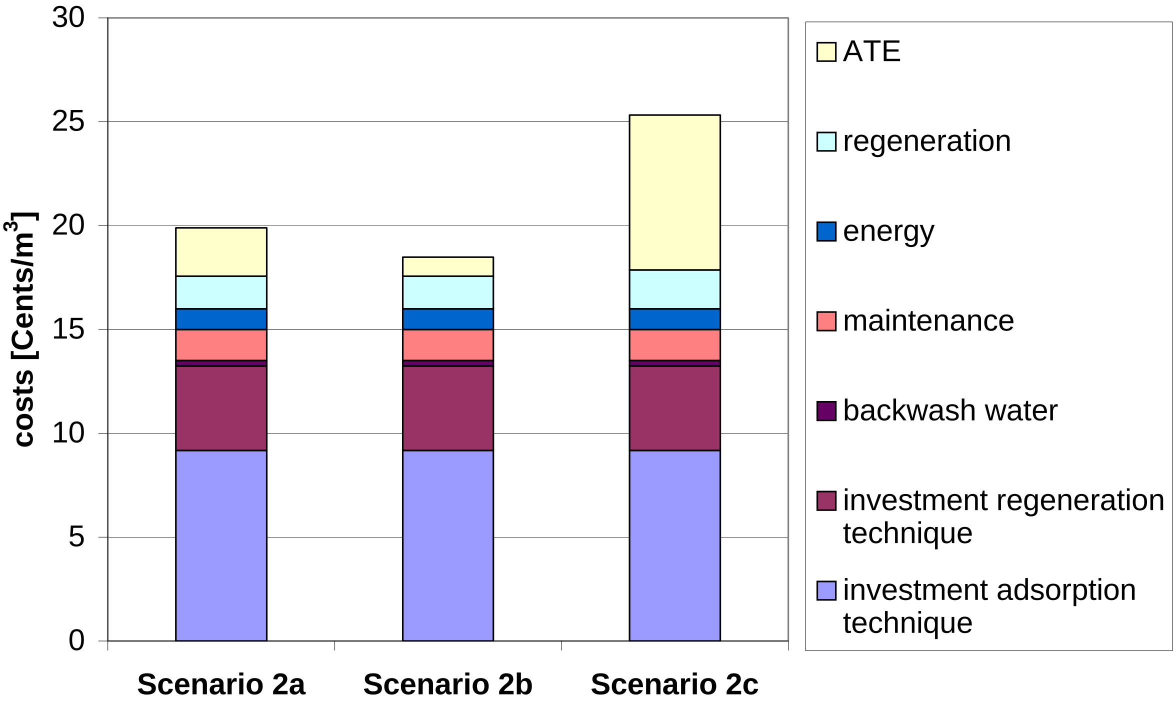

**Fig. 4.2:** Costs in Cents per $m^3$ treated water for ATE-adsorption (10 years of operation) for Scenarios 2a, 2b, 2c.

In **Figure 4.2** results for ATE are shown. Noticeable is the high portion of investment costs (over 50 %) due to the more expensive adsorption and regeneration technique. Compared to GFH, a higher portion of regeneration costs but a significantly lower portion of sorbent costs can be observed. Even in scenario 2c where ATE is disposed after every 13,000 BV still the investment costs are the dominating expense factor.

All calculations were based on an influent P-concentration of 100 µg/L. Assuming an concentration of 300 µg/L, the capacity of GFH and ATE would only amount to 8,000 BV and 4,000 BV, respectively. Therefore, an increase in regeneration and sorbent costs can be expected. Due to more frequent regeneration intervals, regeneration costs would step up:

- regarding GFH from 0.83 to 1.61 Cents/$m^3$ (scenarios 1a and 1b) and from 0.99 to 1.84 Cents/$m^3$ (scenario 1c).
- regarding ATE from 1.57 to 3.22 Cents/$m^3$ (scenarios 2a and 2b) and from 1.87 to 3.67 Cents/$m^3$ (scenario 2c).

However, the portion of regeneration costs would still be small. For example, the total costs for scenario c would step up from 28.65 to 29.51 Cents/m$^3$ for GFH and from 25.32 to 27.11 Cents/m$^3$ for ATE. The higher mechanical stress applied to the material would lead to a more frequent substitute of GFH/ATE. Since long-term experience is lacking, the increase in sorbent costs is hard to estimate.

Evaluating the experimental data (**chapter 3.3**), the assumption of 100 % reloading capacity (scenarios a and b) seems not to be realistic. Effectively one has to consider loss in capacity as well as loss of material. A realistic scenario would be positioned between scenario a and c.

| **Costs per m$^3$ treated water** | **GFH** | **ATE** |
|---|---|---|
| **Investment costs**<br>adsorber, pumps, electronic and regeneration equipment | 3-5 Cents/m$^3$ | 6-9 Cents/m$^3$ |
| **Operating costs**<br>Sorbent | 2-20 Cents/m$^3$<br>(incl. disposal) | 1-8 Cents/m$^3$<br>(excl. disposal) |
| Regeneration | 1-2 Cents/m$^3$ | 2-4 Cents/m$^3$ |
| **Flat valued costs**<br>Energy, maintenance, backwashing | 2-3 Cents/m$^3$ | 2-3 Cents/m$^3$ |
| **Total costs** | **8-30 Cents/m$^3$** | **11-24 Cents/m$^3$** |

**Tab. 4.3:** Summary of estimated costs in Cents per m$^3$ treated water for ATE- and GFH-adsorption (10 years of operation)

The spread of estimated total costs for both ATE- and GFH adsorption is shown in **Table 4.3**. Thereby costs are subdivided in investment, operating and flat valued costs. Operating costs strongly depend on reloading capacity (50-100%), sorbent stability (replacement intervals) and influent P-concentration (0.1 or 0.3 mg/L) and therefore show the largest uncertainty of all costs.

Considering this uncertainty in cost estimation, the price would be somewhere between 8 and 30 Cents per $m^3$ for GFH and between 11 and 24 Cents per $m^3$ for ATE. Generally, ATE adsorption is characterized by smaller sorbent costs but higher investment costs compared to GFH. Costs for GFH adsorption show a significant portion of sorbent costs. Therefore, subject to the condition that regeneration is effective, GFH adsorption would be the favorable technique. Additionally, GFH-adsorbers and tanks for NaOH can be constructed more compact due to the smaller contact time needed. ATE-adsorption could be favorable if no regeneration technique could be established.

## 5 Summary and Outlook

For advanced phosphorus (P) removal sorption processes were studied in bench-scale to offer a post-treatment step in addition to the relatively unknown biological P-removal in membrane bioreactors (MBR) for decentralized wastewater treatment.

First three commercially available sorbents, granulated ferric hydroxide GFH, activated alumina ATE and an iron hydroxide/oxide FER, were screened for their affinity and capacity in removing phosphorus from MBR filtrates.

GFH features the highest loading and affinity for P and additionally removes organics followed by ATE. For example, in determination of isotherms at a P-equilibrium concentration of 0.5 mg/L the loading on GFH amounts to 20 mg/g, on ATE to 9 mg/g and on FER only to 3.8 mg/g. Very early FER was excluded from the trials due to its low capacity and desorption of bonding agents leading to an increase instead of a removal of dissolved organic carbon.

Different influencing parameters were studied in the P-sorption on GFH and ATE. Lowering the pH from 8 to 5 improved the P-sorption only by 30 %. A pH-adjustment for optimization is not recommendable due to the strong buffering of MBR filtrates by the carbonate/hydrogen carbonate system. A decrease in temperature had no effect in P-sorption on GFH at low initial P-concentrations, while the loading on ATE was reduced compared to room temperature. Therefore, an improvement is not expected by an outdoor operation of sorption filters.

No main influencing competition by other organic or inorganic compounds could be determined on P-sorption in MBR filtrates. Due to the negatively charged sorbent surfaces the specifically sorbing phosphorus has an decisive advantage over unspecifically sorbed anions like chloride and sulfate. In time depending experiments lacking of calcium had a kinetic effect on P-sorption, but calcium is present in sufficient amount for P-sorption in MBR filtrates.

In sorption filter tests using bed volumes (BV) around 90 mL a limit value of 50 µg/L P is reached in the effluent at 8,000 bed volumes for GFH and 4,000 for ATE using a influent concentration of 0.3 mg/L P. At a lower influent concentration of 0.1 mg/L P the breakthrough at the limit can be extended to above 15,000 BV for GFH and 8,000 for ATE. While GFH affords a contact time of 10 min, around 30 min contact time is needed in sorption filters filled with ATE to achieve a late breakthrough.

A partial regeneration and P-reloading on GFH and ATE can be achieved by using 0.6 M NaOH in differential recirculating flow reactors. But for several reasons the regeneration can not be transferred to sorption filters directly.

Due to the long operation time of sorption filters at low influent concentrations $\leq$ 0.3 mg/L P the regeneration and reloading could not be studied in sorption filters here. Therefore, the cost estimations could only be based on a few scenarios. Using ATE or GFH, total costs are in the range of 8 - 30 Cents/m³ depending on the possibility of regeneration and reuse of sorbents. If no regeneration can be achieved, an application of ATE would be favoured due to its lower price. Based on an effective regeneration a sorption technique using GFH would be preferable. This is emphasized by the high affinity of GFH for P, which is especially required at low effluent P-concentrations from MBR.

As an outlook it is recommended to verify the sorption performance and to study the breakthrough behavior in a pilot scale ($H = 1$ m, $d \geq 300$ mm). Furthermore, the investigations on regeneration have to be intensified and conducted in sorption filters to assess influencing parameters like the effect of the previous sorption time on regeneration, the regeneration time and concentration of regenerate. The frequency of regeneration and reuse of sorbent until disposal can only be stated by future long-term trials in sorption filters. Due to the low volume flow rate in the small studied sorption filter, which showed no pressure drop during the trials, it is hard to predict if a backwashing is necessary in larger scale. Whether the particle-free MBR filtrate is advantageous for filter operation, in a long-term scale microorganism growth might occur and result in clogging of sorption filters. In this view a regeneration seems to be advantageous and might replace both backwashing and disinfection rinsing.

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