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Removal of free and combined chlorine at GAC surfaces and impact on pool water quality

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Synopsis

In the treatment of swimming pool water, free chlorine is applied for disinfection. Trihalomethanes (THM) and chloramines are the most important disinfection by-products (DBPs) occurring, due to the reaction of free chlorine with organic compounds introduced into the pool by bathers. Many previous studies revealed the health impacts of these substances which necessitate their removal.

Because conventional treatment processes such as flocculation and filtration are insufficient to remove DBPs or precursors, additional treatment with granular activated carbon (GAC) is widely applied in Germany. The objective of the present work is to study the behaviour of combined and free chlorine which are both removed by catalytic reactions at GAC surfaces.

A bench scale plant is set up to measure the performance of both free and combined chlorine species in a pool water cycle by using GAC treatment. The experiments are carried out with several fresh as well as used GACs at controlled pH, temperature and contact time conditions. The reaction rate coefficients determined are related to GAC properties like type of GAC, bed porosity, grain size distribution and BET-surface. Based on the results of lab scale experiments and determined rate coefficients, the effects of different operation regimes are analyzed and discussed.

Introduction

Chlorine-based disinfection is still the most conventional and mainly used way of disinfection, taste and odour control and ammonia removal in swimming pool water treatment. During disinfection free chlorine or hypochlorous acid (HOCl), respectively, reacts with organic nitrogen containing compounds to form DBDs such as chloramines (combined chlorine). For inorganic chloramines a difference can be made between monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3) formed in the following way:

$$NH_3 + HOCl \rightarrow NH_2Cl \quad (1)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 \quad (2)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 \quad (3)$$

Monochloramine is the predominant chloramine species under the typical conditions found in pool water treatment. Due to their impacts on man's health the chloramines concentration should not exceed the threshold of 0.2 mgl^{-1} given by the german regulation DIN 19643.

Various processes have been developed for removing or simply reducing free chlorine residuals from pool water as reviewed by (Olson and Binning 1974; Suidan et al. 1977). Chloramine-removal by granular activated carbon (GAC) appears to be the most common way. Due to catalytic reactions the GAC removes Chlorine and Chloramine over a long period of time effectively.

Reaction mechanism for removal of chloramines by granular activated carbon

The reaction between hypochlorous acid (HOCl) and activated carbon under formation of surface oxides (C*O) can be described by

$$HOCl + C^* \longrightarrow C^*O + Cl^- + H^+ \tag{4}$$

(Snoeyink et al. 1974), where C* represents an active surface area. Caused by the H^+-release the pH-value will decrease. In case of OCl^- as free chlorine species a H^+-release from water or from acid group on the carbon surface was suggested (Olson and Binning 1974). To determine the reaction rates, an assumption was made that the total dechlorination reaction is divided in a reversible adsorption step:

$$C^* + HOCl \underset{k_2}{\overset{k_1}{\rightleftarrows}} CHOCl \tag{5}$$

and a irreversible dissociation under formation of surface oxides:

$$CHOCl^* \xrightarrow{k_3} C^*O + H^+ + Cl^- \tag{6}$$

(Suidan et al. 1977), where CHOCl* represents an adsorbed HOCl molecule.

Reaction mechanism for removal of monochloramine by granular activated carbon

For removal of monochloramine at GAC-surfaces Bauer and Snoeyink (1973) proposed the following reaction:

$$C^*O + 2NH_2Cl \rightleftharpoons C^* + 2H^+ + 2Cl^- + H_2O + N_2 \tag{7}$$

The removal of dichloramine can be described by:

$$2NHCl_2 + H_2O + C^* \rightleftharpoons N_2 + 4H^+ + 4Cl^- + C^*O \tag{8}$$

The free chlorine as well as the combined chlorine removal in a GAC-filter column could be described as a first order reaction of the following form:

$$r(T) = -k(T) \cdot c \quad , \qquad (9)$$

where r(T) is the reaction rate depending on temperature and k(T) the reaction rate constant. For a fixed bed the reaction rate constants can determined by measuring c_{in} and c_{out} at constant flow rates according to:

$$k = \frac{Q}{V_{bed}} \cdot \ln(\frac{c_{in}}{c_{out}}) \quad , \qquad (10)$$

where V_{bed} is the bed volume of the GAC packed bed. The temperature dependence of the reaction constant is given by the Arrhenius law:

$$k(T) = k_0 \cdot e^{-\frac{E_A}{R_o \cdot T}} \quad , \qquad (11)$$

where k_o is the pre-exponential factor, E_A the activation energy and R the universal gas constant.

Experimental Material and Methods

A bench-scale unit (Fig. 1) was used to investigate the reaction rates and reaction constants of free chlorine removal and was subsequently modified for investigation of the chloramine removal.

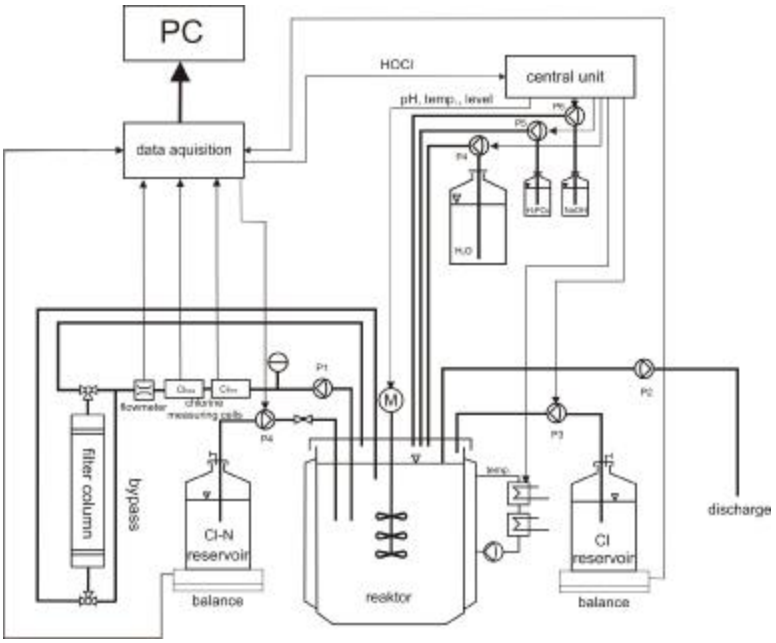

Fig. 1. Modified bench-scale unit for free and combined chlorine removal

The test unit comprises a reactor which held 10 l of deionised water with a feedback controlled HOCl concentration of 4.5 mg l^{-1}. The conductivity was maintained equivalent to typical pool water conditions one-time at 500 µS cm^{-1} using a NaCl solution. Chlorine degraded in the GAC-column was replaced by HOCl solution from a reservoir with known concentrations of 2 mg l^{-1} to maintain the concentration of 4.5 mg l^{-1}. The pH-value was maintained at pH 7 by dosing 10% H_3PO_4 and NaOH solution. The recirculation loop with the embedded filter column was run with a flow rate of 40 l h^{-1} using a Watson-Marlow peristaltic pump. A balance was used to plot the mass-addition of HOCl. The water temperature was kept at 30 or 15 °C using a jacketed reactor whose temperature was controlled by a heating coil or an external cooling system. Initial free and total chlorine concentrations in the filter column were measured online/continuous by membrane-covered, two-electrode sensors. Free and combined chlorine levels for calibrating the sensor were assayed photometric using the conventional Diethyl-p-phenylenediamine (DPD) test. Since equilibrium is attained in the bench scale rig after 1 h of operation the column outlet concentration could indirectly be calculated from a mass balance around the reactor:

$$c_{bed,\,out} = \frac{\left(\frac{dm}{dt}\right)_{Cl,\,res}}{Q_{bed}} \cdot \left(\frac{c_{in,\,bed}}{c_{res}} - 1\right) + c_{in,\,bed} \qquad (12)$$

where dm/dt is the HOCl mass flow rate from reservoir to the reactor, Q is the flow rate, $c_{in,\,bed}$ is the column inlet concentration (equal to the HOCl concentration in the reactor) and c_{res} is the HOCl reservoir concentration. The filter column was filled with 3 Standard and 1 special catalytic granular activated carbon (Table 1).

Table 1. Used carbons

carbon	**time in operation** (months)	**type**
carbon A(12)	12	standard
carbon A(18)	18	standard
carbon B(12)	12	standard
carbon C(12)	12	catalytic activated

The carbons had been in operation in a pilot plant for 12 to 18 months where they where used parallel to the usual pool water treatment process. After application on site the carbons were collected in 10 cm layers over the bed depth of 90 cm. For testing in the bench scale unit 96 ml of dumped carbon volume were filled in the filter column (r=1.7 cm). This equates to 100 mm dumping height in the filter column.

To determine the temperature dependence according to the Arrhenius law trials for the central bed depth (40-50 cm) were carried out at 15 °C and 30 °C.

According to the trials carried out with free chlorine a dilution of 96 % monochloramine and 4 % dichloramine in the reservoir was used to determine the reaction constants for chloramine removal on activated carbon.

The dichloramine to monochloramine ratio was described by a simplified approach neglecting trichloramine (McKee 1960). The monochloramine dilution was prepared freshly for each trial with a Cl_2 to N ratio of 1 to 0.246 (mol/mol) made of equimolar Sodium hypochlorite (NaOCl) and Ammonium chlorite (NH_4Cl) solutions with a concentration of 0.05 mol/l. Hence the Monochloramin reservoir concentration was 2.56 g/l.

Results

Free chlorine removal

Table 2 show the results of column operation under standard experimental conditions at 30°C.
Comparison of the reaction rates determined in this research with rates investigated in earlier studies by Rößler (2005) with the students t-test (5% level of significance) reveals no significant differences in the reaction rate levels. Generally the reaction rate levels for fresh carbons are higher than the levels after usage of 12 or 18 months.
Reaction rate levels for the used standard carbons A(12), A(18) and B(12) range between 0.030 and 0.099 s^{-1}, however the rate constant for the catalytic activated carbon C(12) range between 0.106 and 0.113 s^{-1}.
Consequently dechlorination for the catalytic activated carbon C is more effective than for the standard carbons. This effect can be observed more explicit for the fresh carbons. After usage of 12 and 18 month the two carbons A(12) and A(18) show in average only half of the reaction constant level of carbon C(12). In case of carbon B(12) the difference to the activated carbon C(12) is only poorly developed.

Table 2. Reaction rate constants for free chlorine removal on the fresh and used carbons in s^{-1} (30 °C, pH 7)

carbon / bed depth (cm)	**fresh**	**0-10** (Rößler 2005)	**10-20**	**20-30**	**40-50**	**60-70**
carbon A(12)	0,136	0.057	0.047	*0.030**	0.051	0,050
carbon A(18)	0,136	0.045	0.054	0.055	*0.035**	0.043
carbon B(12)	0,181	0.099	0.095	0.082	0.094	0.084
carbon C(12)	0,384	0.113	0.106	0.106	0.094	0.106

***** outlier as determined by Grubbs test for outliers (95% confidence interval)

The first bed depth in flow direction (0-10 cm) shows consistently higher reaction rate constants for free chlorine removal than those shown in the lower bed depth. Furthermore the results show a constant reaction rate level below the topmost bed depth (0-10 cm) for the used standard

carbons A(12) and B(12) as well as for the activated carbon C(12). It would seem reasonable to attribute these features to the outer GAC-surface (Fig. 2).
As a result of backwashing procedures small GAC-grains accumulate in the top of the bed fixed bed and bigger grains at the bottom. Consequently the external surface area decreases with bed depth. Due to loading and blockage with macromolecular organic material the inner surface is also decreasing with bed depth.

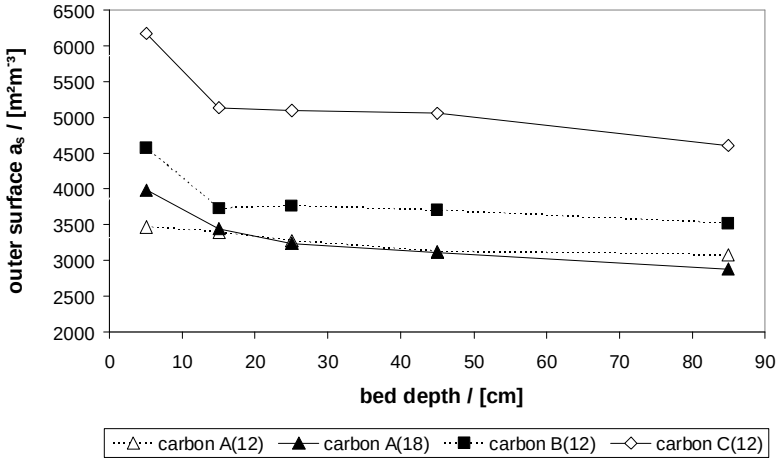

Fig. 2 External and inner surface of the used carbons

Figure 3 respectively shows the ratio of the reaction rate constants and the outer-surface k_s. Obviously the high external surface level in the first bed depth affects the high reaction rate counter wise so that k_s for all carbons shows no trend and differ only in small ranges on a constant level. This implies a direct influence of the external surface on the reaction rate.

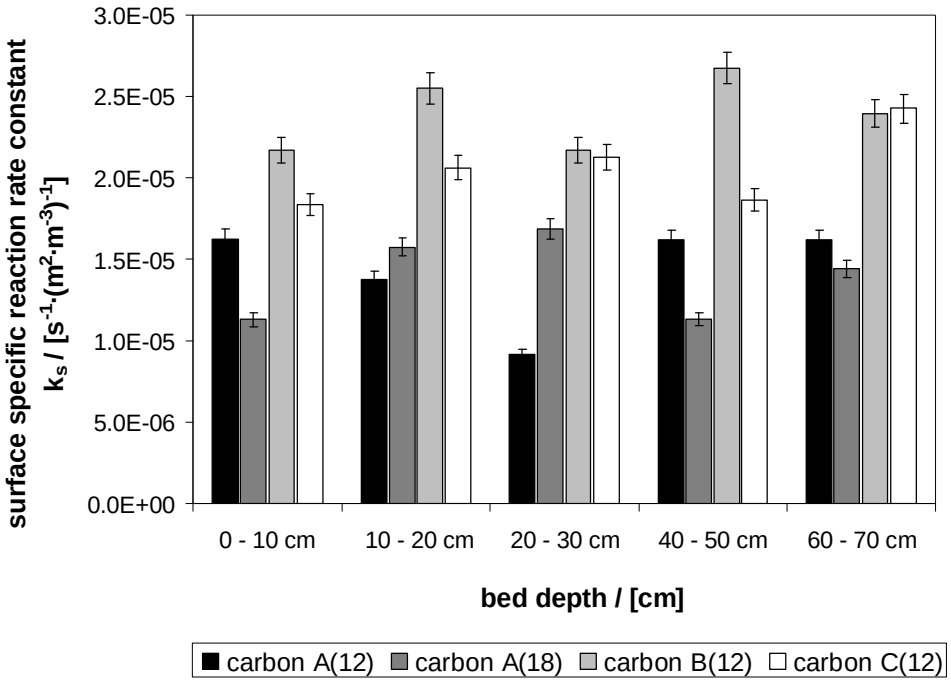

Fig. 3 External surface specific reaction rate constants k_s for free chlorine removal for the used carbons (30 °C, pH 7)

Using the experimentally determined activation energies Fig. 4 shows the simulated reaction rate constants as function of temperature for the fresh and used carbons. In case of the fresh carbons the reaction rate of the catalytic activated carbon C is for the whole temperature scale from 5-40 °C approximately twice as big as the reaction rate of the two standard carbons. After usage of 12 month the reaction rate level of carbon C(12) decreases obviously and matches the values of the standard carbon B. This effect is also shown for the used carbon A(18, 12). The longer used carbon A(18) shows a significant lower reaction rate compared to the sample used only for 12 month.

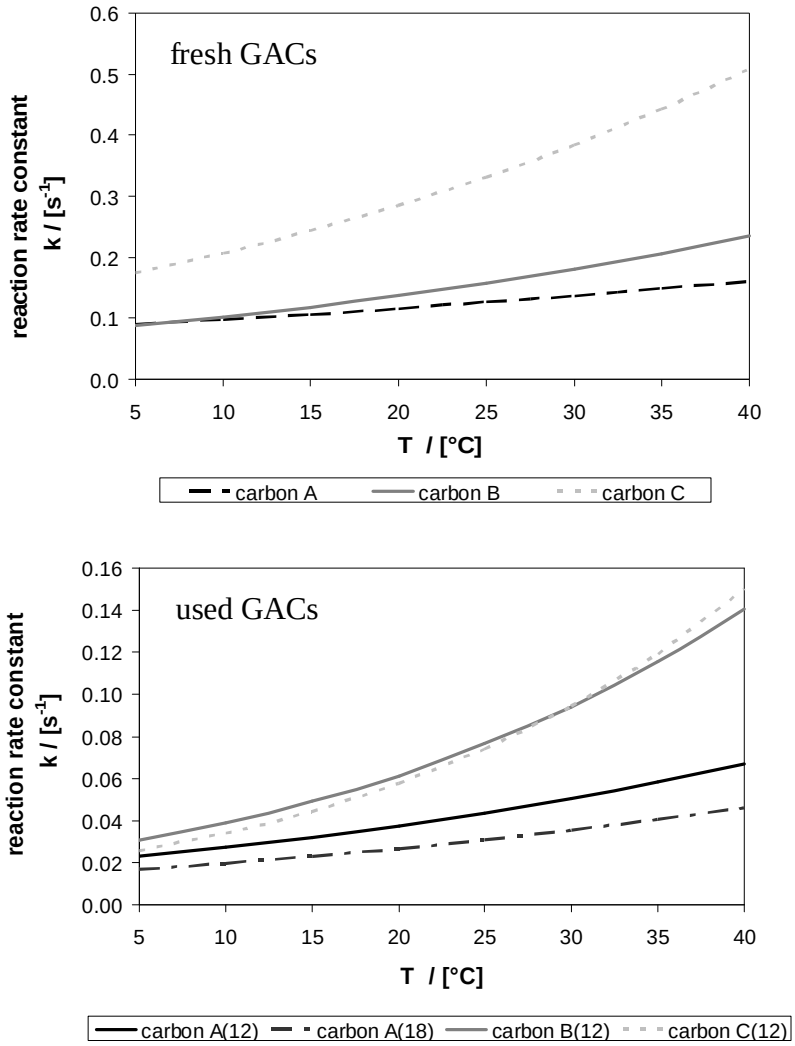

Fig. 4 Temperature dependence on the reaction rate constants for free chlorine removal at the fresh and used carbons (pH 7)

Combined chlorine removal

Currently only the reaction rate constants for the used carbon B(12) and C(12) were investigated (Table 3). Due to monochloramine column outlet-concentrations of zero mgl^{-1} reaction rate constants for the topmost bed depth could not be determined.

Table 3. Reaction rates and rate constants for monochloramine removal for the used carbons B and C (pH 7)

carbon type	bed depth [cm]	temp. [°C]	c_{in} [mgl^{-1}]	c_{out} [mgl^{-1}]	k [s^{-1}]	$r_{GAC,bed}$ [$mgl^{-1}s^{-1}$]
carbon B (12)	0 - 10	30	4,5	*0*	-	-
	20 - 30		4,5	1,07	0,166	0,397
	30 - 70		4,5	0,24	0,340	0,493
	20 - 30	15	4,5	1,62	0,119	0,334
carbon C(12)	0 - 10	30	4,5	*0*	-	-
	20 - 30		4,5	0,09	0,451	0,510
	60 - 70		4,5	*0*	-	-
	20 - 30	15	4,5	2,8	0,084	0,269

However negative concentrations mainly appear in the first bed depth of both carbons wherefore higher reaction rates in this bed layers are assumed to reach the outlet concentration of zero mgl^{-1}.

Temperature dependence on monochloramine removal (Fig. 5) was carried out in a similar way to the free chlorine analysis calculating the constants for the Arrhenius law (eq. 11) using reaction rate constants for the bed depth from 20-30 cm at 15 and 30 °C. For the majority of the temperature scale the catalytic activated carbon C shows higher reaction rate constants compared to those shown by the standard carbon B. Reaction rate constant levels for the standard carbon B seems to have no definite temperature dependence.

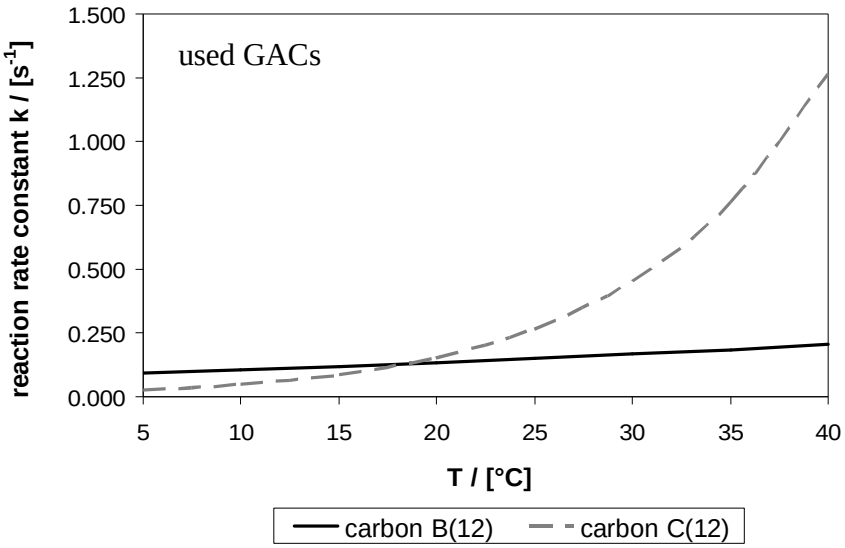

Fig. 5 Temperature dependence on the reaction rate constants for monochloramine removal (pH 7)

Concentration Profiles

Fig. 6 (a,b) respectively show the simulation of a filter column analogue to the used one for laboratory testing measuring 500 instead of 100 mm dumping height.

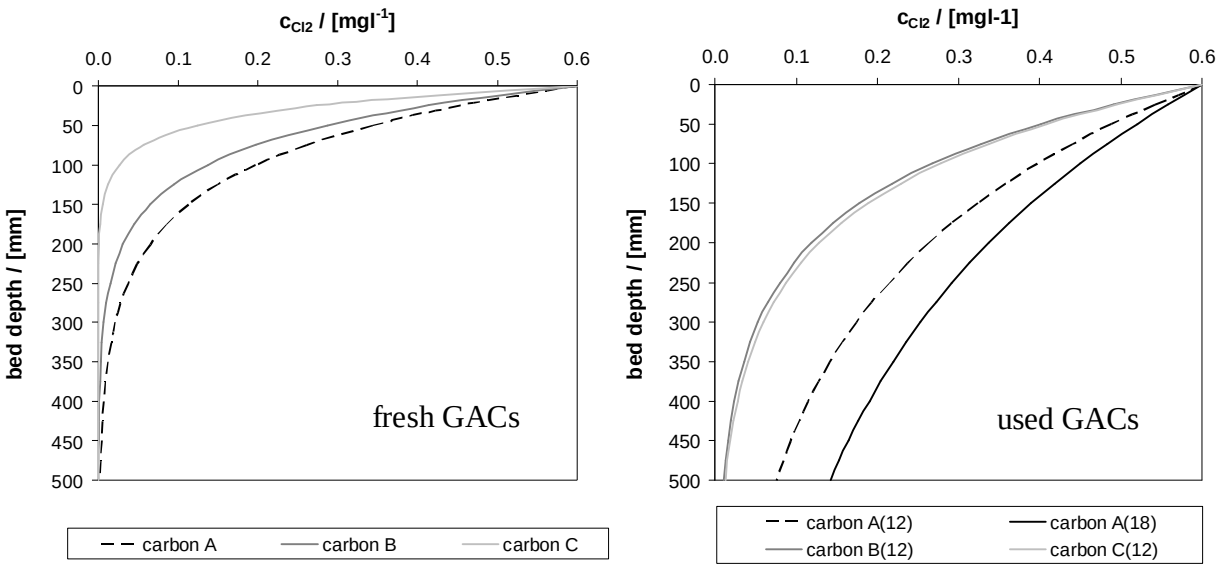

Fig. 6 Concentration profile for free chlorine removal for the fresh and used carbons (30 °C, pH 7)

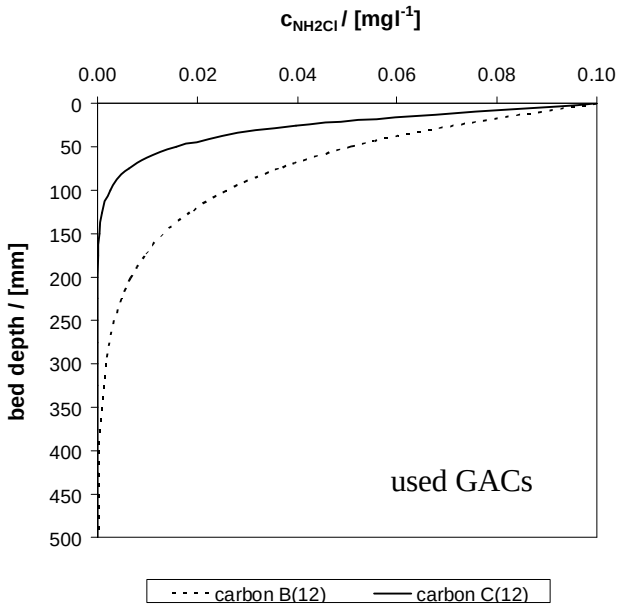

Fig. 7 Concentration profile for monochloramine removal for the used carbons (30 °C, pH 7)

The concentration profiles show for a representative inlet concentration of 0.6 mgl^{-1} free chlorine (Fig. 6 used and fresh) and 0.1 mgl^{-1} combined chlorine (Fig. 7) that for the used carbons all combined chlorine could be removed in bed height of 200 mm (carbon C) to 400 mm (carbon B). However free chlorine remains in the filter-outlet with a maximum concentration of 0.14 mgl^{-1} and a minimum concentration of 0.01 mgl^{-1}
In case of a monochloramine break through in a GAC-filter containing the special catalytic carbon C(12) filling a thin layer of fresh carbon C(12) will remove monochloramine although free chlorine remains in the water as a disinfectant.

Conclusions
The results of this study indicate that the high dechlorination level shown for fresh carbons rapidly decrease with operation time. After 12 to 18 months of operation they show the same rates as fresh carbons and conform to reaction rate levels of standard carbon.
According to higher outer surface levels in the first bed depth in flow direction, all carbons show a higher dechlorination rate as well as carbon B and C show a higher chloramine-removal there. Reaction rates for free chlorine removal show no dependence on the BET-surface. Thus carbons with a smaller grain size distribution hence a high outer-surface is more applicable for dechlorination and chloramine-removal. As expected, the reaction rates for free chlorine and monochloramine removal increase with increasing water temperature. Especially monochloramine removal at the catalytic activated carbon shows a significant temperature dependence explaining a progressive character. Comparison of reaction rate constants determined for free chlorine removal with the constants determined for monochloramine removal show a higher removal rate for monochloramine than for free chlorine. Anyhow, results of filter column simulation indicate that all carbons are able to remove a representative monochloramine concentration of 0.1 mgl^{-1} in used conditions over a bed depth of 150 to 400 mm. Free chlorine is only detected in the filter column outlet for fresh carbons. For this reason chemical dosing for disinfection will decrease with increasing operation time.

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