Modelling GAC adsorption of biologically pre-treated process water from hydrothermal carbonization

J. Fettig and H. Liebe

ABSTRACT

Granular-activated carbon (GAC) adsorption of biologically pre-treated process waters from hydrothermal carbonization (HTC) of different materials was investigated. Overall, isotherms showed that most of the dissolved organic substances are strongly adsorbable while the non-adsorbable fractions are small. The equilibrium data were modelled by using five fictive components to represent the organic matter. Mean film transfer coefficients and mean intraparticle diffusivities were derived from short-column and batch kinetic test data, respectively. Breakthrough curves in GAC columns could be predicted satisfactorily by applying the film-homogeneous diffusion model and using the equilibrium and kinetic parameters determined from batch tests. Thus, the approach is suited to model GAC adsorption of HTC process water under technical-scale conditions.

Key words | activated carbon adsorption, HTC process water, kinetic parameters, modelling

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INTRODUCTION

Hydrothermal carbonization (HTC) is a process that simulates the coalification of biomass by transforming organic material into hydrochar, a material comparable to brown coal. In contrast to the natural process, which takes many years, HTC is finished after less than 12 hours. The HTC process is performed with biomass suspensions in a pressure vessel at 180–220 °C and resulting water vapour pressures of 10–15 bars. After the reaction phase is finished, solid products and process water must be separated by filtration.

According to Ramke et al. (2009), a portion of 15–25% of the input organic carbon is found in the liquid phase. Berge et al. (2011) even report a percentage of 20–37% of the initially present carbon being transferred to the aqueous phase. Thus, recovery and disposal options for the process water must be developed in order to make HTC a feasible process on a technical scale. Usually, HTC process water is acidic, with a chemical oxygen demand (COD) load of 14,000–70,000 mg/L and a biochemical oxygen demand (BOD$_5$) load of 10,000–40,000 mg/L (Ramke et al. 2009). Depending on the input material, considerable amounts of nutrients (N, P and K) might also be encountered (Schneider et al. 2011; Saeta & Tippayawong 2013).

There have been a number of attempts to analyse the organic matter in HTC process water in more detail, but so far the results are qualitative rather than quantitative because of the complex nature of the carbonization process and the impact of both raw materials and process conditions. Ahrens & Martin (2012) listed the following species as some of the main components of the aqueous phase: lactic acid, formic acid, acetic acid, methanol, 1,2-propanediol and 2,3-butanediol. When using rice straw as a raw material, Huang et al. (2013) identified acetic acid and glucose to be the major substances. Poerschmann et al. (2013) found phenols, benzenediols and low-molecular-weight organic acids to be the most abundant components resulting from the carbonization of olive mill wastewater. Stemann et al. (2013) estimated the portion of organic acids in the total organic carbon content to be in the order of 30–50%. In other studies, aldehydes like furfural (Becker et al. 2014; Broch et al. 2014) and even cyanides (Escala et al. 2013) have been detected, thus underlining the need for further treatment.

An earlier study revealed that more than 80% of the initial COD can be removed by aerobic biological treatment (Ramke et al. 2009). This finding was confirmed by Eibisch et al. (2013) who observed that 61–89% of the initial dissolved organic carbon content (DOC) could be mineralized aerobically. However, the energy demand of an aerobic treatment process will be quite high because of the high organic load. Therefore, anaerobic followed by aerobic biological pre-treatment of HTC process water was investigated in the present study using continuously operated laboratory reactors. The details are described elsewhere (Austermann-Haun et al.

2013; Fettig & Liebe 2013). Accordingly, between 84 and 95% of the input organic matter can be removed in the biological stages. However, the remaining non-degradable organics that amount to up to 2,500 mg DOC/L must be removed in a post-treatment stage. This paper focuses on experimental data and modelling of granular-activated carbon (GAC) adsorption of biologically pre-treated HTC process water.

As with many other waters and wastewaters, pre-treated HTC process water contains a large number of organic substances with different adsorbabilities. When describing their adsorption behaviour, it is necessary to divide the mixtures into different components based on their adsorbability. This approach was first proposed by Frick & Sontheimer (1983) using ternary mixtures of a strongly, a weakly and a non-adsorbable component. For industrial wastewaters, the number of components had to be increased in order to obtain a better description (Völker *et al.* 1984). There are a number of models that describe adsorption equilibria in multi-solute systems. A detailed discussion is provided by Sontheimer *et al.* (1988). Accordingly, the ideal adsorbed solution theory (IAST), originally developed for gaseous mixtures and modified for aqueous systems by Radke & Prausnitz (1972), is the most universally applicable model. It is solely based on single-solute parameters, and the Freundlich isotherm has proven to be suitable in this respect (Crittenden *et al.* 1985). Therefore, IAST is well suited for the fictive component approach. In particular, when isotherms are used with a common Freundlich exponent n for all adsorbable components, the calculation is simplified and the number of adjustable parameters can be reduced.

Mass transfer into an adsorbent particle is governed by diffusion processes, which are divided into external mass transfer and intraparticle diffusion. The latter is assumed to occur both in the pores of the adsorbent and along the inner surface in the adsorbed phase (Sontheimer *et al.* 1988). For mixtures of unknown composition, the short fixed-bed reactor technique can be used to determine effective diffusivities that allow an estimation of external mass transfer coefficients from empirical correlations (Cornel *et al.* 1986; Fettig & Sontheimer 1987). Intraparticle diffusivities must be determined from batch adsorption rate curves or fixed-bed breakthrough curves. It is, however, not possible to derive pore and surface diffusion coefficients independently from each other. For the film-homogeneous diffusion model, the intraparticle transport is therefore – as a simplification – assumed to occur completely in the adsorbed phase, thus requiring the determination of one single intraparticle diffusivity. This approach was suited to describe the uptake of humic substances in a technical-

scale fixed-bed GAC adsorber (Hubele 1985), as well as in a bench-scale fixed-bed column of activated aluminium oxide (Fettig 1999). Meanwhile, Crittenden *et al.* (1993) reported that adsorption of natural organic matter in GAC columns could not be predicted satisfactorily. In recent years, the adsorption of mixtures of unknown composition has found little attention. Thus, it was interesting to apply the modelling approach to HTC process water.

MATERIALS AND METHODS

The HTC process water was provided by the waste management and landfill technology section of our university. The process conditions can be found elsewhere (Ramke *et al.* 2013). Three different input materials were studied: spent grains from a brewery, sugar beet residuals and food leftovers.

In this investigation, GAC Norit ROW 0.8 S (Norit Nederland B.V.) was used. It is made from peat; the median particle diameter by weight of the extruded product is 1.18 mm; the particle density is 0.642 g/cm³; and the filter density is 0.374 g/cm³, corresponding to a bed porosity of 0.42. It was applied in granular form for kinetic and column tests. For the isotherm experiments, the carbon particles were crushed in a ball mill. The resulting powdered activated carbon had particle diameters below 40 μm.

Adsorption equilibria were studied by determining overall isotherms (DOC isotherms) by applying the bottle-point method. For each test, between 0.1 and 3.0 g of activated carbon were added to 0.2 L of solution. The pH values were 6.8 (spent grains), 7.8 (sugar beet residuals) and 8.1 (food leftovers), respectively. Previous tests (data not shown) revealed that 72 h of contact time were sufficient to reach equilibrium. After equilibration, the bottles were taken from the shaker, samples were filtered through 0.45 μm membranes and analysed for DOC. Solid-phase DOC concentrations were calculated from a mass balance.

The isotherm data were evaluated using ADSA software (Johannsen *et al.* 1992). Up to five adsorbable components characterized by their Freundlich parameters K_i and n_i are pre-specified, then their initial concentrations $c_{o,i}$ and a non-adsorbable fraction $c_{n.ads}$ are determined by non-linear regression, and IAST is used to model competitive adsorption. For the sake of simplicity, the n_i values are usually assumed as being common for all adsorbable components (Johannsen *et al.* 1992).

The short fixed-bed reactor technique was used in order to determine external mass transfer coefficients for the

organics' uptake by GAC. For this purpose, diluted solutions with an initial DOC concentration of 2–3 mg/L were applied; UV absorbance was used as a surrogate for DOC because the accuracy of the DOC measurement was too low here. From the results, effective diffusivities of the organics, as well as mean film transfer coefficients for other flow rates, were derived. Details of this approach are given by Fettig & Sontheimer (1987). Since all adsorbable components of a mixture are included when this technique is applied, different adsorptivities do not affect the results. The use of UV absorbance as a surrogate for DOC would have an effect on the effective diffusivities derived for the organics only if there were larger fractions in the mixture that had a very high or a very low specific absorbance. However, it is assumed to be unlikely that such fractions are present in biologically pre-treated HTC process water.

Mean intraparticle diffusivities of the organics were determined from DOC concentration-vs-time curves. GAC samples were exposed to the solution in 2 L glass beakers. The carbon particles were placed in a basket attached to a mixing turbine that ensured a superficial flow rate through the basket of about 100 m/h. External mass transfer coefficients were estimated for this flow rate from effective diffusivities. Then, the film-homogeneous diffusion model was fitted to the experimental data, assuming the same value of the intraparticle diffusivity for all adsorbable components.

Column experiments were conducted with two glass columns, 3 cm in diameter and 50 cm high, which were operated in series. Each column was filled with 27.5 cm of GAC. The process water was pumped to a constant head tank to feed the columns at a constant rate corresponding to a filter velocity of 0.8 m/h. Such low values are not unusual for GAC columns operated with high inlet concentrations and small flow rates. A typical example is the GAC treatment of landfill leachates (Fettig *et al.* 1996). These boundary conditions also apply to HTC process water.

The total empty bed contact time was about 41 minutes. The DOC breakthrough curves were compared with data predicted by the film-homogeneous diffusion model using the isotherm and kinetic parameters determined from batch tests.

The DOC concentrations were measured with a TOC-Analyser 5050 (Shimadzu Corp., Kyoto, Japan), and UV absorbance was determined with a UviLine 9400 spectrophotometer (SI Analytics, GmbH, Mainz, Germany). pH was measured with a pH meter 539 (Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). All experiments were conducted at room temperature of 22 °C.

RESULTS AND DISCUSSION

Overall isotherms of pre-treated HTC food leftovers process water for two different initial concentrations are shown in Figure 1. Accordingly, quite high solid-phase concentrations of more than 150 mg DOC/g were obtained, proving that the major portion of the organics is fairly well adsorbed by activated carbon. Meanwhile, the shifting of the isotherm with decreasing initial concentration towards higher solid-phase concentrations indicates that species with different affinities to the carbon surface, i.e., different adsorbabilities, are present in the process water.

The data were evaluated by selecting one non-adsorbable fraction corresponding to the Freundlich coefficient $K_1 = 0$, and four adsorbable fractions corresponding to $K_2 = 10$, $K_3 = 30$, $K_4 = 60$ and $K_5 = 80$, respectively, with the Freundlich exponent being $n = 0.2$, and fitting the IAST model to both isotherms simultaneously. The idea was to use one set of parameters for all three process waters. As a fitting criterion, the minimization of the relative deviations between calculated and measured aqueous-phase concentrations, as well as solid-phase concentrations, was used (Johannsen & Worch 1994). Previous trials (data not shown) were conducted with other sets of K values and with only three adsorbable components, but in both cases significantly larger deviations were obtained. Therefore, the approach to use five components altogether, i.e., to fit five adjustable parameters $c_{o,i}$ to 16 isotherm data per type of water, was considered a proper compromise. The results obtained are listed in Table 1.

The IAST model is a theory based on molar concentrations of the components. Since these data cannot be determined in a mixture of unknown composition, it is assumed that molecular weight is the same for all adsorbable components when the calculations are conducted
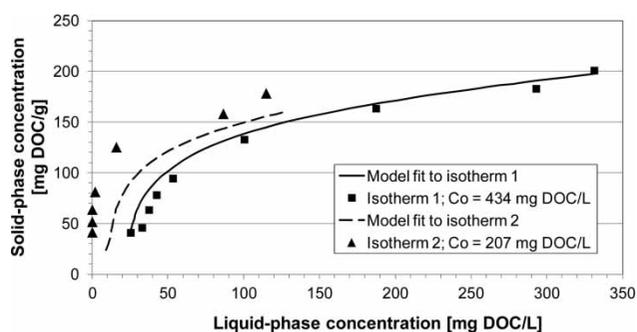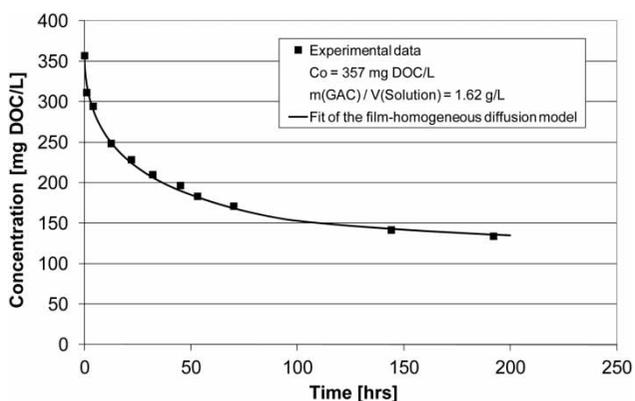
Figure 1 │ Adsorption isotherms of pre-treated HTC food leftovers process water and fit of the IAST model.

Table 1 │ Fractions of five fictive components derived from overall isotherms for pre-treated HTC process water (K_1–K_5 and n are the Freundlich isotherm parameters of each component)

Component	Input material		
	Spent grains (%)	Sugar beet residuals (%)	Food leftovers (%)
1: $K_1 = 0$	0.99	0.87	3.81
2: $K_2 = 10$ mg/g (L/mg)$^{0.2}$; $n = 0.2$	0.84	0	2.42
3: $K_3 = 30$ mg/g (L/mg)$^{0.2}$; $n = 0.2$	0	15.36	4.84
4: $K_4 = 60$ mg/g (L/mg)$^{0.2}$; $n = 0.2$	89.77	83.77	73.24
5: $K_5 = 80$ mg/g (L/mg)$^{0.2}$; $n = 0.2$	8.40	0	15.69

Table 2 │ Effective diffusivities $D_{L,\text{eff}}$, mean molecular weights M_W, mean film transfer coefficients β_L for a filter velocity of 0.8 m/h, and mean intraparticle diffusivities D_S for pre-treated HTC process water

Parameter	Input material		
	Spent grains	Sugar beet residuals	Food leftovers
$D_{L,\text{eff}}$ (m^2/s)	1.9×10^{-10}	1.3×10^{-10}	1.6×10^{-10}
M_W (Dalton)	1,480	3,150	2,080
β_L (m/s)	0.34×10^{-5}	0.25×10^{-5}	0.30×10^{-5}
D_S (m^2/s)	1.2×10^{-13}	1.1×10^{-13}	1.1×10^{-13}

with mass concentrations. However, the components' molecular weights will then be incorporated into their K-values (Sontheimer et al. 1988). The parameters given in Table 1 reveal that the non-adsorbable fractions are very small (about 0.9–3.8%), while the major fraction is found for the Freundlich coefficient $K_4 = 60$. This means that most of the organics are quite strongly adsorbable. Therefore, an adsorption stage that is designed adequately should be able to remove most of the organic matter from process water remaining after biological pre-treatment.

Adsorption rate data for HTC food leftovers process water are presented in Figure 2. The intraparticle diffusivities determined from such rate data are given in Table 2, together with the effective diffusivities $D_{L,\text{eff}}$ derived from the short fixed-bed column tests. The latter parameters were further used to estimate mean molecular weight data M_W for the adsorbable organics according to the following equation proposed by Sontheimer et al. (1988):
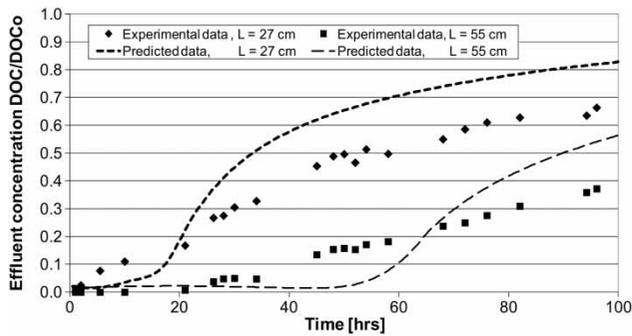
$$D_{L,\text{eff}} = 7,3 \times 10^{-9} \times M_W{}^{-0,5} (\text{m}^2/\text{s})$$

According to the data, the mean molecular weight differs between about 1,500 Dalton for spent grains as an input material, and more than 3,000 Dalton for pre-treated process water from sugar beet residuals. Thus, the organic substances remaining after biodegradation are considerably larger than low-molecular-weight compounds (acids, alcohols) regularly found in raw process water. Their mean size is of the same order as the size of aquatic humic substances (Fettig 1999). In HTC process water from carbonization of sucrose, about 50% of the dissolved organic matter was estimated to be larger than 1,000 Dalton (Weiner et al. 2012). Therefore, both larger molecules in raw process water and transformations during biodegradation are assumed to contribute to the mean molecular weight data observed.

The intraparticle diffusivities are quite similar; however, their absolute values must always be discussed in the context of the kinetic model applied. Compared to data from the literature, the diffusivities resemble parameters obtained for humic substances rather than parameters determined for low-molecular-weight organics (Sontheimer et al. 1988).
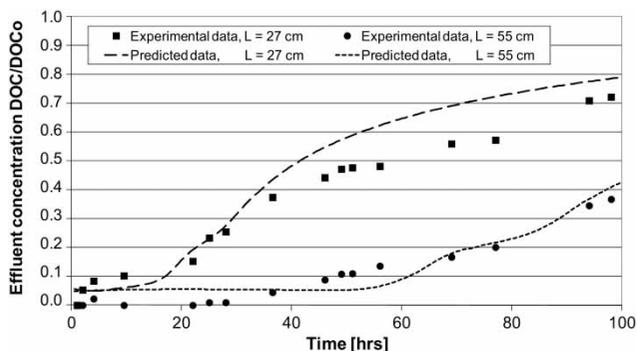
A comparison between experimental and predicted breakthrough curves is shown in Figures 3–5. The predictions are solely based on the parameters given in Tables 1 and 2. Although there are some differences between the data obtained for a short-bed length, the initial breakthrough and the column capacities, which were calculated from the amount of organics adsorbed at the end of the column test and the total mass of GAC, are predicted quite well. As shown in Table 3, the maximum deviation between experimental and predicted column capacities for 55 cm of bed length is 6.7%. Therefore, it can be concluded that the film-homogeneous diffusion model, in combination with the multi-component approach for the description of the

Figure 2 │ Adsorption rate curve of pre-treated HTC food leftovers process water on granular Norit ROW 0.8 S.

Figure 3 | Experimental and predicted breakthrough curves of pre-treated HTC spent grains process water.
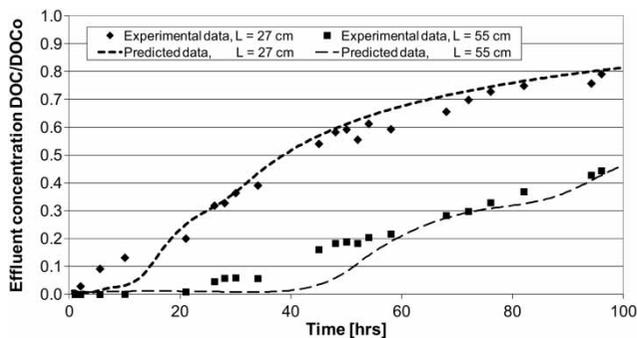
Figure 4 | Experimental and predicted breakthrough curves of pre-treated HTC sugar beet residuals process water.

Figure 5 | Experimental and predicted breakthrough curves of pre-treated HTC food leftovers process water.

adsorption equilibria, is suited to predict the performance of technical-scale GAC adsorbers for the post-treatment of HTC process water, and to determine the most appropriate operating conditions.

An example for the simulation of a technical-scale GAC column treating HTC spent grains process water is given in Figure 6. It was assumed that three columns with 2 m of bed length each are operated in series. Since the weakly adsorbable component ($K_2 = 10$) represents only 0.84% of the total mixture, it was lumped together with the non-adsorbable fraction in order to avoid numerical problems. The major fictive component ($K_4 = 60$), accounting for almost 90% of the process water's organics, determines the breakthrough curve that rises rather steeply after about 1,300 hours. As illustrated by the components' breakthrough curves, the 'tail' of the overall breakthrough is due to the continuous uptake of the most strongly adsorbable component ($K_5 = 80$). According to the simulation results, average solid-phase concentrations, i.e., carbon loadings calculated from the amount of organics adsorbed at 1,300 hours and the total mass of GAC, of the order of 200 mg/g DOC, will be obtained. However, long contact times are required in order to utilize GAC with the highest possible efficiency, first of all because of slow uptake rates. The spent carbon can be reactivated under conditions similar to those used for its activation, and then reused after the combustion losses have been replaced by fresh carbon.

CONCLUSIONS

1. Adsorption onto activated carbon is well suited to remove organics from HTC process water remaining after anaerobic and aerobic degradation. The adsorption equilibria can be described by applying the IAST model and a fictive component approach. The non-adsorbable fractions are small, and the major components are quite strongly adsorbable.

Table 3 | Comparison between experimental and predicted column capacities

	Input material					
	Spent grains		Sugar beet residuals		Food leftovers	
Parameter	Column 1	Column 1 + 2	Column 1	Column 1 + 2	Column 1	Column 1 + 2
Experiment capacity (mg DOC/g)	166.9	136.6	139.6	110.2	167.3	123.5
Predicted capacity (mg DOC/g)	153.2	136.0	137.4	117.6	146.5	122.8
Deviation (%)	−8.2	−0.4	−1.6	+6.7	−12.4	−0.6
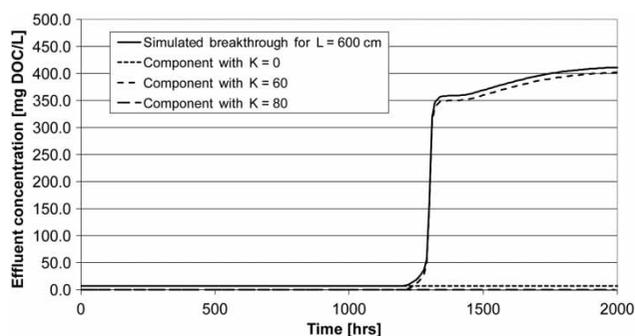
Figure 6 │ Predicted breakthrough curve of pre-treated HTC spent grains process water in a technical-scale GAC column; conditions: bed length 6 m (3 columns in series), empty bed contact time 7.5 hours, influent concentration 420 mg DOC/L.

2. The uptake rates on GAC are rather slow. Effective diffusivities estimated from short-column data indicate that average molecular weights are between 1,500 and more than 3,000 Dalton. Intraparticle diffusivities derived from batch tests are of the same order as kinetic parameters found for humic substances.

3. Breakthrough curves in GAC columns can be predicted satisfactorily by the film-homogeneous diffusion model using the multi-component approach in order to describe adsorption equilibria and mean kinetic parameters determined from batch data.

4. Simulations reveal that carbon loadings of up to 200 mg DOC/g can be obtained in technical-scale GAC columns operated with long contact times.

ACKNOWLEDGEMENT

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