Hydrothermal treatment for regeneration of activated carbon loaded with organic micropollutants

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Abstract

Hydrothermal treatment (HT) at 200°C and 240°C for 4 and 16 h was studied for the regeneration of granular activated carbon (AC) loaded with a range of organic micropollutants having a broad range of physico-chemical properties. Carbamazepine, diazinon, diclofenac, estrone, iohexol, metoprolol and sulfamethoxazole were fully converted. Limits were seen for the conversion of caffeine, ibuprofen and perfluorooctanesulfonate (PFOS). However, the degree of degradation was enhanced for the latter compounds in the adsorbed state as compared to experiments in aqueous solution. The methodology was tested in five loading and regeneration cycles for selected compounds with no change of the degradation potential and of the AC properties. In particular, the surface properties of the AC did not deteriorate upon HT as determined by the specific surface area (from BET isotherms), the point of zero charge, and the surface functional groups (from diffuse reflectance IR spectroscopy). As the total concentration of the loaded pollutants was minimized by HT, this method could be considered as a new low temperature regeneration technology for spent AC.

Keywords

activated carbon – hydrothermal treatment – wastewater treatment – organic pollutants

1 Introduction

A wide variety of organic micropollutants has been globally detected in waterbodies due to their inefficient removal in wastewater treatment plants (WWTP) [1]. Despite their low concentrations in the ng L^{-1} to µg L^{-1} range, large effects on water organisms have been identified, for example due to estrogenic activities of hormones and endocrine-disrupting chemicals [2,3]. As these contaminants are not completely removed by current biological processes in WWTP, new treatment methods are being discussed and implemented [4]. One suggestion is the use of activated carbons (ACs) as adsorbent in order to remove micropollutants in a post-biological treatment step [4]. Adsorption is governed among other factors by the polarity of the sorbate, its concentration and loading, as well as the properties of the AC [5]. Granular ACs have been tested for cleaning of drinking water and for WWTPs in separate tanks subsequent to the biological treatment [6,7,8]. Loaded granular AC has to be either regenerated after use or incinerated [9]. One currently employed method is the thermal activation with water vapour or CO_2 at temperatures up to 800°C [9,10]. The sorbed contaminants are desorbed or decomposed (pyrolysed) under these conditions. However, this regeneration method is rather costly and yields little advantage over the cost of fresh AC. Another studied regeneration method for removal of organic pollutants from AC is the wet air oxidation process at temperatures between 150 and 250°C for 2 to 4 h [11,12,13]. The mild reaction conditions are economically advantageous; however, the ACs deteriorate with regard to their specific surface area due to the loss of micropores and a total mass loss. When powdered AC is added to the biological treatment in the WWTP and mixed with the sewage sludge, it can only be incinerated for destruction of the pollutants [14]. Thus, there is a need for alternative and more economical regeneration technologies.

An alternative idea is to regenerate loaded ACs by a HT process at moderate temperatures of 200-260°C in aqueous suspension under elevated pressure. This method could be suitable for removal of the adsorbed contaminants, as these are desorbed, transformed and destroyed under hydrothermal conditions [15]. In a recent study it was shown that a wide variety of chemicals can be decomposed under hydrothermal conditions (255°C), albeit in aqueous solutions [16]. Similarly, the concentration of a cocktail of polar pharmaceuticals was significantly degraded during hydrothermal carbonization (HTC) of sewage sludge at 210°C [17]. Based on these previous studies, temperatures of 200°C and 240°C were chosen in the present study for AC regeneration.

A variety of organic pollutants with a range of sorption affinities was loaded onto a commercial granular AC. The selection of the pollutions was based on their prominence as typical contaminants occurring in WWTPs and their receiving water bodies: the pharmaceuticals carbamazepine, diclofenac, ibuprofen, metoprolol and sulfamethoxazole, iohexol as contrast agent prominent in hospital effluents, estrone as degradation product from synthetic hormones, caffeine, the pesticide diazinon, the corrosion inhibitor 1H-benzotriazol and the perfluorinated surfactants perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS).

The potential of HT for the degradation of pollutants was studied via subsequent extraction of the AC and analysis of the degree of conversion as well as the formation of potential metabolites by GC-MS and HPLC. One goal of this study was to evaluate the role of the sorbent AC for the degradation of selected compounds. In order to study whether sorption on AC enhances or inhibits the degradation reactions, additional experiments for comparison were carried out in aqueous buffered solution, i.e. in the absence of sorbents. In order to avoid misinterpretation we use the term ‚degradation' in this study for any *chemical conversion* of the target compounds

74 down to complete mineralization but including the formation of metabolites. The term
75 degradation does not include the removal of target compounds from the aqueous system just by
76 volatilization or adsorption.

77 In a recent publication, it has been shown that AC played a double role during HT of triclosan:,
78 namely as adsorbent and as co-reactant [18]. A further aim was to apply several regeneration
79 cycles and study the surface properties of the AC by measurement of the BET surface area, the
80 point of zero charge (PZC), and surface functional groups – the latter by means of diffuse
81 reflectance infrared spectroscopy (DRIFT). The novelty of this work is the low cost regeneration
82 of activated carbon without changing the properties of the AC in a significant way.

83

2 Experimental

2.1 Chemicals. Stock solutions of organic chemicals were prepared in acetone, chloroform, or methanol as indicated in Table S1. Acetone and dichloromethane were from Th. Geyer (puriss, 99 %). 2,6-Dichloroaniline, acetonitrile (HPLC grade), carbamazepine, caffeine, diazinon, the sodium salt of diclofenac, estrone, formic acid, ibuprofen, iohexol, metoprolol, PFOA, PFOS, phenol-d_6, and sulphamethoxazole were from Aldrich. 2,6-Dichlorodiphenylamine, 2-chloro-N-methylaniline and benzotriazole were purchased from Alfa Aesar. *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA), and phenanthrene-d_{10} were from Supelco. Ammonium acetate, chloroform, $Na_2HPO_4 \bullet 2H_2O$, methanol, potassium hydroxide, sodium chloride, sodium sulfate, sulphuric acid, silica gel, and toluene were from Merck, the solvents being GC-MS grade. 1-(2,6-dichlorophenyl)-3H-indolin-2-one was from Fluorochem, and 1-methylbenzotriazole from Chempur. Millipore water was generated in-house and used for adsorption experiments. Granular activated carbon (POOL W, 1.5-3.5 mm, CarboTech GmbH, Essen, Germany) was washed at least five times with Millipore water in order to remove residual chloride. Properties of the analysed compounds and AC are summarized in the SI part (Tables S1, S2 and S3).

2.2 Extraction experiments. Prior to extraction experiments, the AC was loaded as described in 2.3. After the two days shaking the AC was separated by centrifugation and extracted by various procedures as described in Table 2. The extracts were analysed by means of GC-MS or HPLC coupled to a DAD detector, or by means of UPLC-MS/MS for PFOS and PFOA. The obtained recoveries are summarized in Table 1. For extraction of aqueous solutions (centrifugates or buffer solutions, see 2.4), 1 mL of the aqueous phase was extracted with dichloromethane (2 x 0.5 mL, containing phenanthrene-d_{10} and phenol-d_5 as internal standards), dried over Na_2SO_4,

filtered over a silica plug and analysed per GC-MS (see Table S1). Extraction experiments were done at least three times.

2.3 Adsorption experiments. AC (50 mg) suspensions were prepared in Millipore water (5 mL) and an aliquot of the organic chemical stock solution (50-100 µL of approximately 5 g L^{-1} stock solution) was added, resulting in an AC loading of about 1 wt-%. The suspensions were slightly shaken for two days. In order to test the degree of adsorption, an aliquot of the aqueous phase was removed by syringe, filtered over a silica plug and either a) analysed per HPLC, or b) extracted as described in 2.2. The degree of adsorption was determined as >99 % for all chemicals under study. All adsorption experiments were done at least two times.

2.4 Hydrothermal treatment. The organic compounds (about 100 mg L^{-1} from stock solutions, Table S1) were given in glass vials with a) an AC suspension (5 mL, 10 g L^{-1} of AC) or b) an aqueous phosphate buffer (5 mL, pH 7, 0.01 M). Additional acetone (≤ 1 mL, based on the co-solvency power of acetone) was added to the aqueous suspensions or aqueous phosphate buffer if the water solubility of the target compound (for estrone) was exceeded, in order to ensure a homogeneous solution. For the experiments in acidic or alkaline milieu the initial pH of the solution or suspension was adjusted with H_2SO_4 or NaOH. The AC suspensions were gently shaken for 48 h and the pH was readjusted. All suspensions and solutions were transferred into glass tubes and placed in in-house designed stainless steel autoclaves (i.d. 16 mm, o.d. 20 mm, length 100 mm), flame-sealed, placed in a GC-oven (Shimadzu GC-14A) and heated to 200°C or 240°C for 4 or 16 h. For PFOS degradation, a reaction temperature of 260˚C was held for 16 h. During the HT the autoclaves were overhead-rotated (60 rpm, in-house constructed rotator) in order to ensure an extensive mixing of the suspensions. Autoclaves were opened after cooling to room temperature to avoid a possible loss of the solution due to the elevated inside pressure. An

aliquot of 0.5 mL was taken from the aqueous phase for IC analysis of the halide ion concentrations. In the cases of AC suspensions, the phases were separated by centrifugation. The aqueous phase was filtered over a silica plug and either analysed by means of HPLC or extracted as described in the 2.1. The aqueous phosphate buffer solution was treated similarly. The separated AC was treated as described in 2.1 and Table 2. Prior to GC-MS analysis the organic extracts were derivatised with BSTFA (+50 µL, heating to 80°C for 1 h) yielding trimethylsilyl derivatives of hydroxyl and carboxyl groups.

For testing whether the AC can be regenerated multiple times, the AC was loaded with a mixture of selected pollutants (carbamazepine, diazinon, iohexol, metoprolol, and sulfamethoxazole, 1 wt-% each), followed by HT at 240°C for 4 h. After 5 loading-regeneration cycles, the AC was extracted and analysed for residual pollutants and degradation products as described in 2.1.

All hydrothermal conversion experiments were done at least two times.

2.5 GC-MS analysis. A QP 2010 Plus GC-MS (Shimadzu) was used, equipped with a HP 5 MS column (length 30 m, i.d. 0.32 mm, film thickness 0.25 µm). The injector and ion source temperatures were 250°C. Method A: 1 µL of sample was injected with a split ratio of 5:1. The GC oven program was as follows: 40°C held for 5 min, with a linear temperature gradient of 8 K min^{-1} up to 200°C and held for 12 min. Method B: 0.5 µL of sample was injected with a split ratio of 5:1. The GC oven program was as follows: 40°C held for 5 min, with a linear temperature gradient of 8 K min^{-1} up to 280°C and held for 10 min. Data acquisition was in full scan mode in the *m/z* range from 33-550 amu. The GC-MS retention times and characteristic *m/z* values for the monitored compounds can be found in Table S1. Quantification of components was performed based on relative response factors of the individual compounds to the internal

standards phenanthrene-d_{10} (*m/z* = 188) or phenol-d_5 (*m/z* = 99). When no reference was available for the transformation products, they were semi-quantified via the response factors of their respective parent compounds.

2.6 HPLC analysis. HPLC was performed on a Hewlett Packard HPLC (HP 1100) with a Gemini-C18 column (4.6 x 250 mm, 5 µm, 110 Å, Phenomenex, Torrance, CA) using a diode array detector (at 254 and 270 nm). The column temperature was 30°C. The aqueous samples were analysed with the following gradient method at a flow rate of 1 mL min^{-1} using mixtures of MeOH and water with 0.1 % formic acid as mobile phase. Initial solvent composition at *t* = 0 min was 30 : 70 MeOH : H_2O, which was held for 3 min, then changed over 1 min to MeOH:H_2O 80:20 (*t* = 4 min), and held for 6 min (*t* = 10 min), before returning to MeOH:H_2O 30:70 in 1 min (*t* = 11 min) and held for 4 min (*t* = 15 min). Quantification was performed by external calibration of the respective analytes in a concentration range from 1-100 mg L^{-1}. PFOS and PFOA solutions were filtered through a syringe filter (PTFE, 0.45 µm, Minisart, Sartorius) and analysed by means of UPLC-MS/MS using dilutions of the solutions after adding mass-labelled standards. Chromatographic separation was achieved using an Acquity UPLC I-class (Waters, Milford, MA, U.S.) equipped with an Acquity UPLC BEH Shield RP18 (1.7 µm, 2.1 x 50 mm) column, followed by mass analysis on a Xevo-TQ-S Triple QMS (Waters) in negative electrospray ionization mode. The UPLC gradient method used a flow rate of 0.4 mL min^{-1} with 2 mM NH_4OAc in H_2O (A) and MeOH (B) as mobile phase. The initial solvent composition at *t* = 0 min was 90:10 A:B, held for 0.5 min, then changed over 4.0 min to 35:65 A:B (*t* = 4.5 min), then changed over 4.75 min to 20 : 80 A : B (*t* = 8.25 min), then in 0.01 min to 0.01 : 99.9 A : B (*t* = 8.26 min), and held for 2.74 min (*t* = 11 min), before returning to 90 : 10 A : B in 0.01 min (*t* = 11.01 min), and held for 3.99 min (*t* = 15 min). MS was run in Multiple

Reaction Monitoring (MRM) mode with a capillary voltage of 1 kV and desolvation temperature of 350°C. The cone voltage was 2 or 30 V and the collision energy 12 or 38 V for PFOA and PFOS, respectively. Quantification was performed by adding isotope labelled internal standards perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid and perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonic acid.

2.7 Halide ion analysis. Halide ion concentrations were analysed on an IC DX 500 ion chromatograph (Dionex) equipped with an anion suppressor (ASRS300), conductivity detector (IC 25) and an IonPac AS11-HC column (4 x 250 mm) using a flow rate of 1 mL min^{-1} and gradient elution with the following program for chloride and fluoride analysis: 1 mM KOH from 0-8 min, increase linearly to 30 mM KOH over 20 min and held at 30 mM KOH for 2 min. For iodide ions: 1 mM KOH from 0-8 min, increase linearly to 30 mM KOH over 20 min and held at 30 mM KOH for 10 min. Prior to analysis, the samples were filtered over a silica plug and diluted with Millipore water if necessary.

The pH value was measured with a pH meter (MP 225, Mettler Toledo, Gieβen, Germany).

2.8 AC characterization. Surface area and pore size distribution were determined with the Brunauer-Emmet-Teller (BET) method on a BelsorpIImini (Belsorp Japan Inc.) by N_2-adsorption/desorption at -196°C. The AC samples were pre-dried at 200°C in vacuum. For measuring the PZC, the AC (1 mg) was placed in a vial containing 5 mL of 0.01 M NaCl solution. The concentration of the AC was increased stepwise. The suspensions were shaken overnight after each addition of AC, and the resulting pH was measured. The final point was reached when the pH of the suspension did not change significantly upon addition of further AC portions. DRIFT was performed on a Bruker Vector 22 spectrometer. The AC samples were diluted 30 times by grinding with solid KBr and analysed at 30°C under N_2-flow (220 mL min^{-1}).

The number of scans was 50 over a wavenumber range from 4000 to 600 cm^{-1} with a resolution of 4 per cm^{-1}.

3 Results and Discussion

3.1 Results for the hydrothermal degradation of pollutants

Hydrothermal treatments of loaded ACs were performed at 200°C for 4 h and 16 h, as well as at 240°C for 4 h when incomplete removal of the pollutants was obtained at 200°C. For comparison, the same treatment was performed in aqueous buffered solution at pH 7 (pH measured at 20°C). Results are presented in Figures 1 to 3.

Diazinon was fully removed by HT at 200°C for 4 h, independently of the reaction medium (Figure 1a-b). The rapid conversion can be attributed to a fast hydrolysis of the thiophosphoester moiety.

The degree of conversion was enhanced by the presence of AC for carbamazepine, estrone, iohexol, metoprolol and sulfamethoxazole under mild HT conditions (HT at 200°C). The largest effect was seen for sulfamethoxazole, for which adsorption increased the conversion from 30 % in aqueous solution to 98 % in AC suspension (Figure 1a-b). Sorbed iohexol and metoprolol were converted to >99 % under mild conditions, while conversion of carbamazepine, estrone, and sulfamethoxazole could be enhanced to >99 % at elevated reaction time and temperature. Even at treatment under harsh conditions (HT at 240°C), 6 % of metoprolol remained in aqueous buffer solution (Figure 1b).

Sorption on AC increased the initial conversion of iohexol. In aqueous solution, the release of iodide was almost 100 % under harsh conditions while only 80 % were released in AC suspension (Table S4). This finding is in line with some iodine/iodide capture by the AC.

The results obtained herein for carbamazepine are in line with findings from vom Eyser et al., in which carbamazepine present in a sewage sludge suspension showed a conversion of >90 % after HT at 210°C for 4 h [17]. However, the HT herein show much higher conversion of metoprolol in AC suspension or buffer solution than in the presence of sewage sludge [17].

Benzotriazol was only degraded at prolonged reaction times of 16 h or at increased temperatures in the presence of AC (Figure 1a), whereas it is highly reactive in the freely dissolved state. It reacts with a strange kinetics: 10 % conversion after 4 h and 98 % after 16 h at 200°C with AC. Upon HT in buffer solution at 200°C for 4 h, methyl-benzotriazole (68 ± 3 %) was formed by methylation of benzotriazole at one of the nitrogen atoms due to reaction with methanol introduced as a solvent of stock solutions (Figure 1b). When adsorbed onto AC, no methylation of benzotriazole was observed. Methyl-benzotriazole proved more recalcitrant towards degradation than 1H-benzotriazol.

Diclofenac was fully converted under all the applied conditions (Figure 1a-b). These findings are comparable to literature data [16]. Several chlorinated degradation products were identified (Figure 2). In AC suspensions, only one product, dichlorodiphenylamine, was identified, while in buffer solutions several products were formed (Figure S1). Indolin-2-one, whose concentration amounted to 50 % of the initial diclofenac concentration after HT at 200°C and 240°C, could be formed via intramolecular amide formation (Figure 2). At high temperatures, dichloroaniline and chloro-*N*-methylaniline were formed. The chloride concentration, quantified after HT of AC suspensions, was only 5-10 % of the chlorine content in diclofenac (Table S4). This finding

indicates that other unidentified chlorinated products were formed and were not detected by the applied GC-MS method. Despite the high degree of conversion, the detection of recalcitrant chlorinated metabolites is unsatisfactory with regard to their potential toxicity.

Caffeine and ibuprofen were not completely degraded under any of the applied conditions (Figure 1a-b). These findings are in line with data from Weiner et al. [16] and vom Eyser et al. [17], in which during hydrothermal carbonization of sucrose and sewage sludge also no complete removal of ibuprofen was observed. In aqueous solution, no conversion was seen even under harsh reaction conditions (see comparison to ibuprofen recovery of 77 %, Table S1). Adsorption onto AC seemed to enhance the conversion of both ibuprofen and caffeine at prolonged reaction times and enhanced temperature. In order to evaluate the influence of the solution pH on the conversion of adsorbed caffeine and ibuprofen, additional experiments were carried out at pH 4 and 10 at 240°C (Figure 1c). A maximum of 60 % of caffeine and 80 % of ibuprofen were converted, with only minor effects of the pH values.

Surprisingly, PFOA was converted to >99 % in the presence as well in the absence of AC at 200°C for 4 h. HPLC-MS/MS analysis did not reveal the formation of short-chain perfluorinated carboxylic acids (C4-C7), which are known as typical products from oxidative treatment with sulfate radicals [19]. The fluoride content in the solutions was <1 % of the stoichiometric amount, thus almost no defluorination occurred (Table S4).

As PFOS is known to be stable even at high temperatures [20], a severe HT at 260°C for 16 h was applied. In neutral buffer solution, PFOS was not significantly converted, while in the presence of AC about 50 % of PFOS was eliminated under strongly acidic conditions (pH 1, Figure 3). At alkaline pH of 12, no degradation of PFOS was observed, even in the presence of AC. The remaining PFOS is distributed between the two states, dissolved and adsorbed,

depending on the pH. The sorption equilibrium is mainly controlled by the pH-dependent AC surface state rather than by the PFOS speciation. Even at pH 1, the PFOS molecule is mainly in its deprotonated form (Table S3). However, the speciation of PFOS may change at high temperatures. HPLC-MS/MS analysis did not reveal the formation of perfluorinated carboxylic acids (C4-C8) or shorter-chain perfluorinated sulphonic acids. The released fluoride content was 7 % for HT at pH 1, while all other conditions yielded fluoride concentrations below the limit of detection (Table S4).

3.2 Discussion

At present it is unknown whether the degradation of the investigated pollutants occurs in the adsorbed state or in solution. In a previous study on the catalytic effect of AC on the hydrolysis of chlorinated organic compounds, it was suggested that hydrophobic organic compounds adsorbed on AC were accessible for hydrophilic species such as water and hydroxyl ions [21]. Furthermore, it was proposed that during wet oxidation of pollutants loaded on AC, the pollutants were oxidized in the adsorbed state and the more polar or gaseous products were then desorbed [22]. Thus, it might be likely that the hydrothermal degradation of pollutants also happens in the adsorbed state, because for most of the studied pollutants the presence of AC enhanced the degree of conversion; benzotriazole and diclofenac were exceptions. For benzotriazol the kinetics were unexpected and the reaction in solution was faster than in AC suspension. Possibly, the transfer from the (protected) adsorbed state to the (reactive) dissolved state may be a slow step. As expected, HT, even under severe reaction conditions, is not suitable for mineralization of perfluorinated alkyl chains, as perfluorinated compounds are known to be highly persistent [4]. But a decrease in PFOA concentration could be observered. So under HT conditions decarboxylation of PFOA could lead to the formation of fluorinated alkanes (e.g. 1H-

perfluoroheptane), which are highly volatile and would escape from the aqueous phase. Decarboxylation of the carboxyl radical $C_7F_{15}COO\bullet$ gives rise to an unzipping reaction pathway leading to the formation of shorter-chain fluorinated acids [19], which were not detected. However, the presumed decarboxylation reaction under HT conditions probably proceeds via a non-radical mechanism. Further analysis would be necessary in order to identify the fluorinated products. For PFOS degradation under acidic conditions a small deflourination as observes. This finding indicates that a partial defluorination (about 1.2 fluoride ions per PFOS molecule) had occurred at pH 1, possibly initiated via removal of the sulfonate group [23]. Further and detailed analyses would be necessary prior to optimizing PFOS degradation.

In order to evaluate the presented novel regeneration method for AC, the formation of potentially harmful metabolites should be considered. However, for most of the studied pollutants, metabolites were not traced. This is partially due to the applied analysis method, GC-MS, which is not suitable for detection of very polar compounds. Thus, a final statement on the achievable detoxification cannot be made. However, in a previous study we could show that adsorption of triclosan on AC hindered the formation of chlorinated dioxins, whereas the latter were formed during HT in aqueous solutions [18].

3.3 Characterization of the AC after hydrothermal regeneration

In order to test the stability of the AC under hydrothermal conditions, it was heated in aqueous suspension at 200°C for 4 h at various initial pH values (2, 4, 7, 10, 12) and at 240°C for 4 h at pH 7. The pH dropped after HT in all suspensions (Table 3). Additional characterizations of the AC loaded with pollutants and treated at 200°C or 240°C for 4 h were performed. The re-use of the AC in 5 subsequent regeneration cycles was studied by loading with selected pollutants (carbamazepine, diazinon, iohexol, metoprolol, and sulfamethoxazole, 1 wt-% each), followed

by HT at 240°C for 4 h. After 5 cycles, the AC was extracted and analysed for pollution conversion. All pollutants were converted to >99 %.

Table 3 shows the surface areas obtained upon BET measurements. The untreated AC has a specific surface area of 860 m^2 g^{-1}. After HT, all specific surface areas were in the range between 800 to 900 m^2 g^{-1}. The specific surface increased only slightly after HT of AC in alkaline medium (pH 12). Thus, one can conclude that HT does not significantly reduce or increase the internal surface area of AC.

The PZC gives information about surface functional groups, such as Bronsted acidic or basic sites. The PZC of the original AC was 7.6. After HT of AC suspensions with moderate pH values (4-10), the PZC was shifted to slightly higher values (Table 3). This finding indicates a loss of acidic surface groups, such as carboxylates, during HT. Significant changes on the AC were observed after treatment under strongly acidic (initial pH of 2) and strongly alkaline conditions (initial pH of 12). However, these changes could be due to small amounts of residual (adsorbed) acids or bases inside the pores rather than surface groups [24]. When pollutants had been present during HT, no significant change was observed for the PZC as compared to unloaded AC.

DRIFT spectra of all of the above mentioned ACs were recorded (Figures S2, S3, S4). All spectra show absorption bands between 2400 to 2300 cm^{-1} and 1600 to 1500 cm^{-1} corresponding to O-H and C-O vibrations in carboxylic groups, respectively [25]. In treated AC, the band for the O-H stretching vibration shows two maxima, indicating the presence of a new kind of carboxylic groups. No differences were seen among the various treatments or in loading with pollutants (Figure S2, S3).

In summary, the characteristics of the AC were only marginally influenced by HT. Under all the applied conditions, no significant loss of AC mass was observed. Using the AC in 5 subsequent loading and regeneration cycles did not reveal changes in the adsorption properties of the AC.

4 Conclusions

The results of the present study show that regeneration of AC by hydrothermal treatment is possible, as most of the pollutants studied were degraded under harsh reaction conditions. However, some exceptions were seen for caffeine, ibuprofen, PFOS and triclosan [18]. The conversion degrees of organic compounds were higher for most pollutants in the presence of AC than in an aqueous buffer solution at pH 7. Although we do not know the actual extent of adsorption under reaction conditions, the effect of AC must be assigned to an enhanced reactivity of adsorbates. Thus, AC seems to support a range of reactions, such as hydrolysis and decarboxylations [22]. In contrast, some dehalogenation reactions seemed to be inhibited when pollutants were loaded on AC. This accounted for diclofenac and possibly iohexol conversion, where the released halide concentrations were higher after HT in buffer solution. PFOS and PFOA do not release fluoride under the applied reaction conditions ($T \leq 240°C$). For an enhanced conversion of organic pollutants, especially for converting chlorinated and fluorinated aromatic compounds, a wet oxidative treatment for regeneration of the AC could be considered. Initial experiments have shown that wet oxidation with molecular oxygen (O_2) as oxidant can lead to dechlorination and complete conversion of chlorinated phenols and naphthalenes [26]. By hydrothermal treatment of AC at 240°C, the concentrations of most of the pre-loaded pollutants were significantly reduced. As the properties of the AC were not adversely affected by the treatment, hydrothermal regeneration could be taken into consideration as a resource-efficient

option. Different kinds of AC, such as powdered AC, or granular AC that were made from different materials and by other preparation methods, should be studied in the future as the origin of the AC can influence its reactivity for chemical conversion of sorbates.

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the Internet at

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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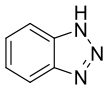
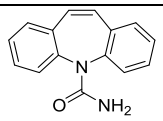
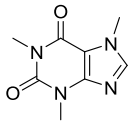
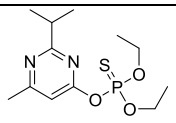
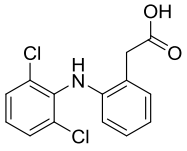
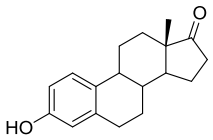
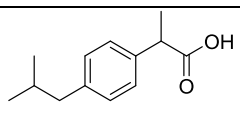
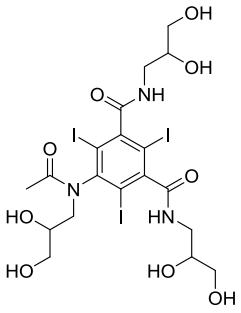
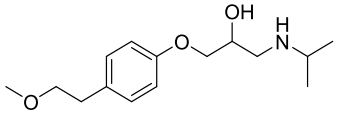
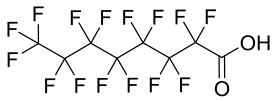
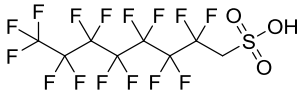
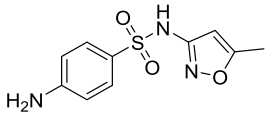
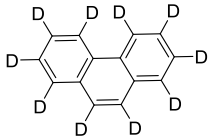
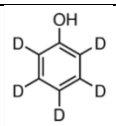
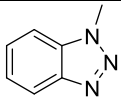
374 **Table 1.** Names and structures of investigated compounds, applied extraction and analytical
375 methods, extraction recoveries from activated carbon. The initial AC loading was the same in all
376 samples, about 1 wt%.

Compound	**Structure**	**Analysis method**	**Extraction method[a]**	**Recovery from AC [%]**
1H-Benzo-triazole		GC-MS[A]	A	114 ± 2[b]
Carba-mazepine		HPLC-DAD	D	99 ± 4
Caffeine		GC-MS[A]	C	80 ± 5
Diazinon		HPLC-DAD	E	97 ± 2
Diclofenac		GC-MS[A]	C	100 ± 15
Estrone		GC-MS[B]	B	129 ± 10
Ibuprofen		GC-MS[A]	C	70 ± 2

Iohexol		HPLC-DAD	D	77 ± 4
Metoprolol		HPLC-DAD	D	65 ± 10
PFOA		HPLC-CAD	F	108 ± 2
PFOS		HPLC-CAD	G	88 ± 4
Sulfamethoxazole		HPLC-DAD	D	69 ± 1
Phenanthrene-d_{10}		GC-MS[A]	-	-
Phenol-d_5		GC-MS[A]	-	-
1-Methylbenzo-triazole[c]		GC-MS[A]	-	-

377 [a] Assignment of the extraction methods is given in Table 2. [b] Mean deviation of individual values
378 (at least 3) from the mean value. [c] Identified metabolite from benzotriazole. [A] Analysed with GC-
379 MS method A. [B] Analysed with GC-MS method B.

380

381 **Table 2.** Extraction procedures applied for the various analytes from activated carbon

Analytical method	ID	Procedure	Analytes
GC-MS	A	MeOH and toluene (2 mL + 2 mL), an internal standard (0.1 mg as stock solution) and KOH (1 mg) were added to the AC (50 mg), and the suspension was shaken for 24 h. An aliquot (1 mL) was dried over Na_2SO_4 and filtered over a silica plug.	benzotriazole
GC-MS	B	Toluene (4 mL) and an internal standard (0.1 mg as stock solution) were added to the AC, and the suspension was shaken for 24 h. An aliquot (1 mL) was dried over Na_2SO_4 and filtered over a silica plug.	estrone
GC-MS	C	MeOH and toluene (2 mL + 2 mL) and an internal standard (0.1 mg as stock solution) were added to the AC, and the suspension was shaken for 24 h. An aliquot (1 mL) was dried over Na_2SO_4 and filtered over a silica plug.	caffeine, diclofenac, ibuprofen
HPLC-DAD	D	MeOH and toluene (2 mL + 2 mL) were added to the AC, and the suspension was shaken for 24 h. The suspension was filtered over a silica plug, the solvents were evaporated to dryness and the residue taken up in H_2O (5 mL).	carbamazepine, iohexol, metoprolol, sulfamethoxazole

HPLC-DAD	E	Acetonitrile (15 mL) was added to the AC, and the suspension was shaken for 24 h. The suspension was sonicated for 20 min and filtered over a silica plug.	diazinon
HPLC-MS/MS	F	MeOH (20 mL) was added to the AC, and the suspension was shaken for 24 h. The suspension was filtered over a silica plug, an aliquot (0.5 mL) taken and diluted with 2 mM NH_4OAc solution (0.5 mL).	PFOA
HPLC-MS/MS	G	MeOH (50 mL) was added to the AC, and the suspension was extracted in a Soxhlet apparatus for 48 h. The suspension was filtered over a silica plug, an aliquot (0.5 mL) taken and diluted with 2 mM NH_4OAc solution (0.5 mL).	PFOS

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383

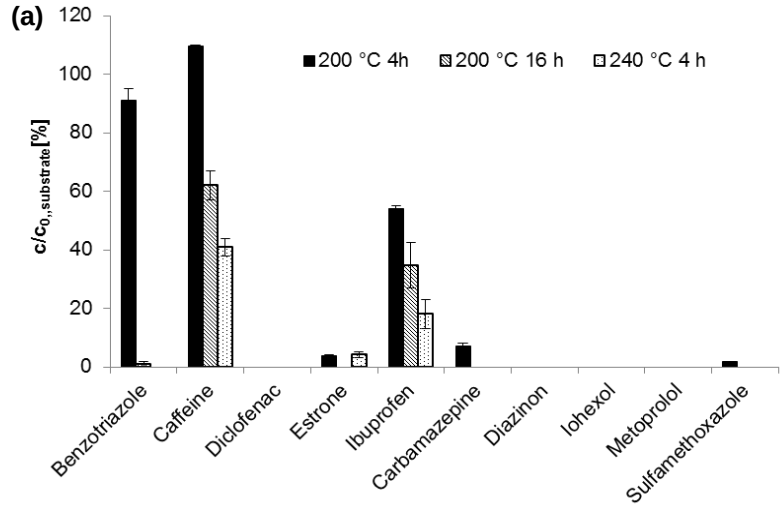
384 **Table 3.** Properties of ACs after hydrothermal treatment (t = 4 h for all samples).

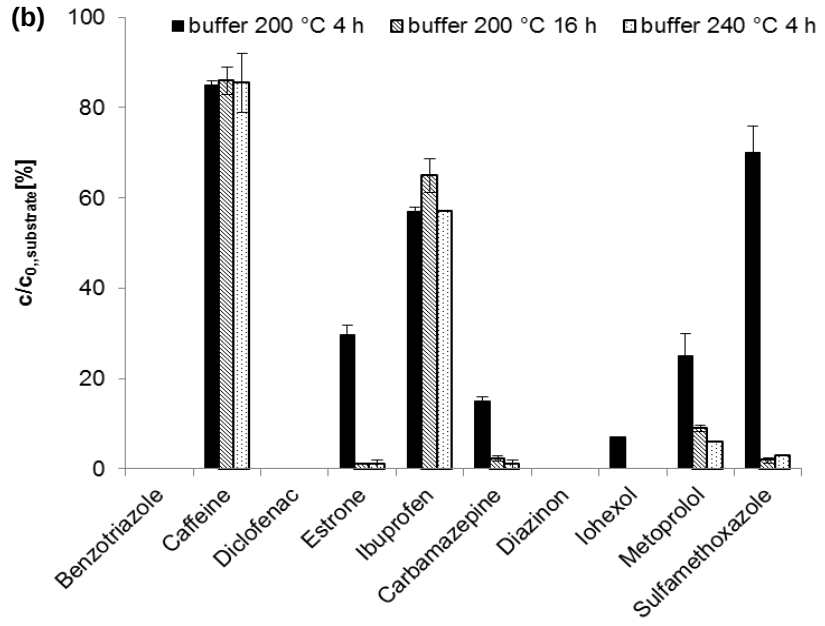
Experiment, initial pH	**pH after HT**	**BET surface area [m^2 g^{-1}]**	**pH_{PZC}**
Initial AC	-	860	7.6
200°C, pH 2	1	836	<1.8
200°C, pH 4	3	821	8.1
200°C, pH 7	4	901	8.2
200°C, pH 10	4	898	8.3
200°C, pH 12	9	940	>10.2
240°C, pH 7	-	817	8.3
200°C, pH 7, + pollutants	-	807	8.0
240°C, pH 7, + pollutants	-	864	8.3
240°C, pH 7, + pollutants, 5 cycles	-	878	7.9

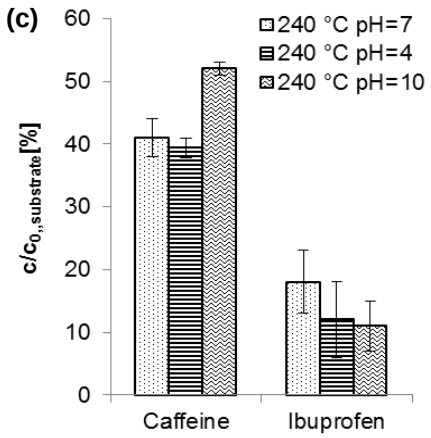
385

386

Figure 1. Residual concentrations of pollutants after hydrothermal treatment, normalized to the initial concentrations in a) AC suspension of 10 g L^{-1} at pH 7, b) 10 mM phosphate buffer at pH 7, and c) AC suspension of 10 g L^{-1} at pH 4, 7, and 10 at 240°C for 4 h. Error bars correspond to mean deviations among individual runs from the average values. 'Missing' columns correspond to negligible remaining concentrations (c/c_0 < 1 %).





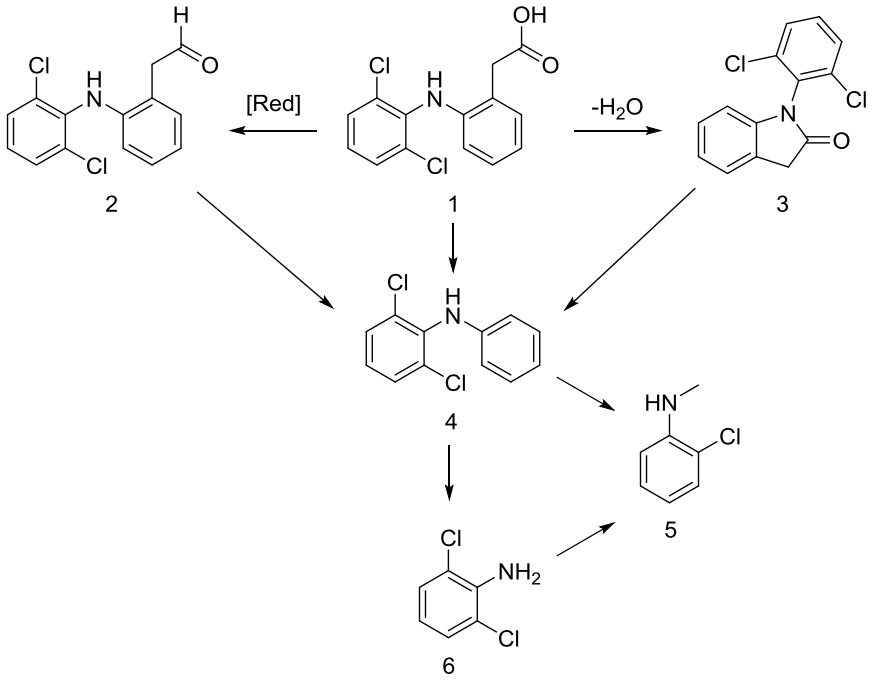

(c)
60
50
40
30
20
10
0
240 °C pH=7
240 °C pH=4
240 °C pH=10
c/c0,,substrate [%]
Caffeine
Ibuprofen

394

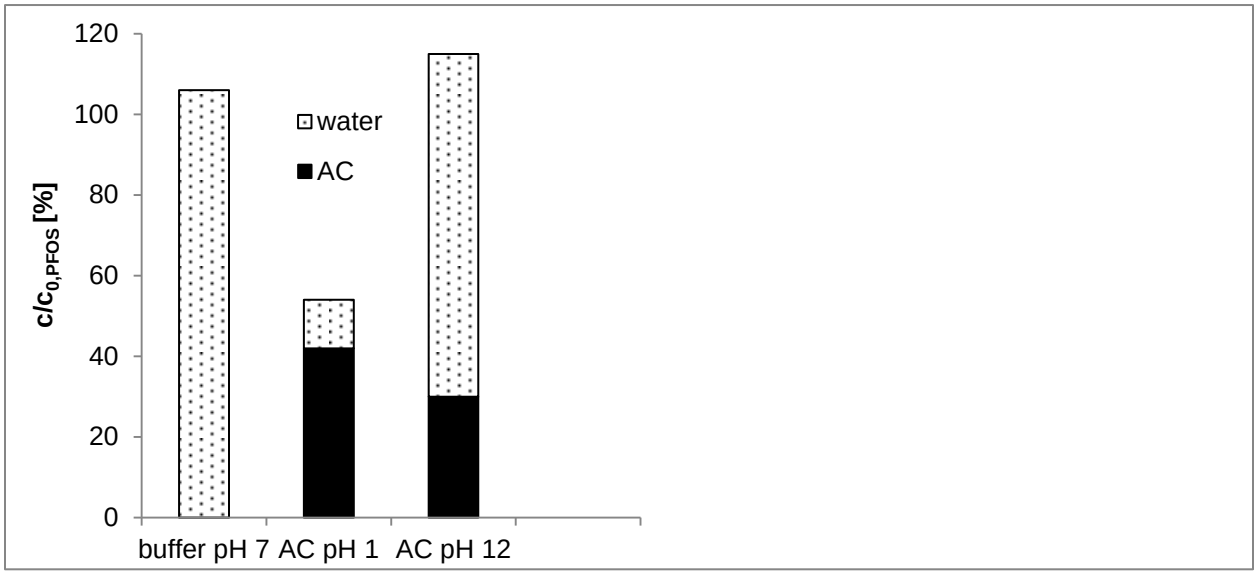
395

396

Figure 2. Proposed reaction mechanism for the hydrothermal degradation of diclofenac (1) to aldehyde (2), indol-2-one (3), dichlorodiphenylamine (4), chloromethylaniline (5), and dichloroaniline (6).



404 **Figure 3.** Residual concentrations of PFOS after hydrothermal treatment at 260°C for 16 h
405 normalized to the initial concentration. Distribution among AC and water phase (at 20°C) is
406 shown. The concentrations were corrected for extraction recoveries from AC (88 %) and for
407 adsorption on the glass surface (about 30 %).



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