



Hydrothermal treatment for regeneration of activated carbon loaded with organic micropollutants

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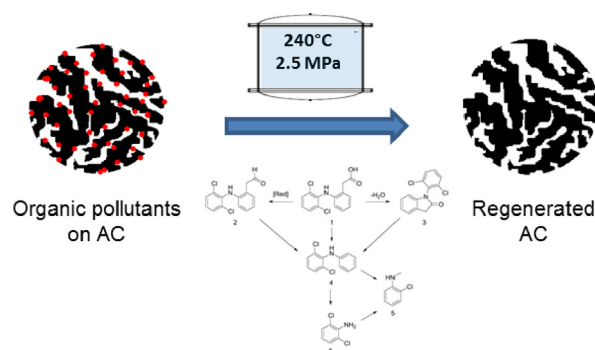
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HIGHLIGHTS

- Spent granular activated carbon was regenerated by hydrothermal treatment.
- The role of the sorbent for degradation of selected organic compounds was studied.
- Conversion of pollutants was higher in the presence of AC than in aqueous solution.
- Hydrothermal treatment of AC at 240 °C reduced the pollutant concentrations.
- The surface properties of the AC were not adversely changed.

GRAPHICAL ABSTRACT



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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.

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1. Introduction

A wide variety of organic micropollutants has been globally detected in waterbodies due to their inefficient removal in wastewater treatment plants (WWTP) (Reemtsma et al., 2006). Despite their low concentrations in the ng L^{-1} to $\mu\text{g L}^{-1}$ range, large effects on water organisms

have been identified, for example due to estrogenic activities of hormones and endocrine-disrupting chemicals (de Mes et al., 2005; Körner et al., 2000). As these contaminants are not completely removed by current biological processes in WWTP, new treatment methods are being discussed and implemented (Joss et al., 2008). One suggestion is the use of activated carbons (ACs) as adsorbent in order to remove micropollutants in a post-biological treatment step (Joss et al., 2008). Adsorption is governed among other factors by the polarity of the sorbate, its concentration and loading, as well as the properties of the AC

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(Li et al., 2002). Granular ACs have been tested for cleaning of drinking water and for WWTPs in separate tanks subsequent to the biological treatment (Babi et al., 2007; Gerrity et al., 2011; Reungoat et al., 2012). Loaded granular AC has to be either regenerated after use or incinerated (Wastewater Technology Fact Sheet Granular Activated Carbon Adsorption and Regeneration, 2000). One currently employed method is the thermal activation with water vapour or CO₂ at temperatures up to 800 °C (Wastewater Technology Fact Sheet Granular Activated Carbon Adsorption and Regeneration, 2000; Waer et al., 1992). 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 (Salvador et al., 2015; Ledesma et al., 2015; Delmas et al., 2009). 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 (Boehler et al., 2012). 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 (Akiya & Savage, 2002). 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 (Weiner et al., 2013). Similarly, the concentration of a cocktail of polar pharmaceuticals was significantly degraded during hydrothermal carbonization (HTC) of sewage sludge at 210 °C (Vom Eyser et al., 2015). 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 pollutants 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 down to complete mineralization but including the formation of metabolites. The term degradation does not include the removal of target compounds from the aqueous system just by volatilization or adsorption.

In a recent publication, it has been shown that AC played a double role during HT of triclosan, namely as adsorbent and as co-reactant (Weiner et al., 2017). A further aim was to apply several regeneration cycles and study the surface properties of the AC by measurement of the BET surface area, the point of zero charge (PZC), and surface functional groups – the latter by means of diffuse reflectance infrared spectroscopy (DRIFT). The novelty of this work is the low cost regeneration of activated carbon without changing the properties of the AC in a significant way.

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-d₆, 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-d₁₀ were from Supelco. Ammonium acetate, chloroform, Na₂HPO₄·2H₂O, 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 Section 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 Section 2.4), 1 mL of the aqueous phase was extracted with dichloromethane (2 × 0.5 mL, containing phenanthrene-d₁₀ and phenol-d₅ as internal standards), dried over Na₂SO₄, 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 Section 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 H₂SO₄ 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

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