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Adsorption of Organic Stormwater Pollutants onto Activated Carbon from Sewage Sludge

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Abstract

Adsorption filters have the potential to retain suspended pollutants physically, as well as attracting and chemically attaching dissolved compounds onto the adsorbent. This study investigated the adsorption of eight hydrophobic organic compounds (HOCs) frequently detected in stormwater – including four polycyclic aromatic hydrocarbons (PAHs), two phthalates and two alkylphenols – onto activated carbon produced from domestic sewage sludge. Adsorption was studied using batch tests. Kinetic studies indicated that bulk adsorption of HOCs occurred within 10 min. Sludge-based activated carbon was as efficient as tested commercial carbons for adsorbing HOCs; adsorption capacities ranged from 70 to 2800 µg/g ($C_{initial}$=10–300 µg/L; 15 mg SBAC in 150 mL solution; 24 h contact time) for each HOC. In the batch tests, the adsorption capacity was generally negatively correlated to the compounds' hydrophobicity (log K_{ow}) and positively associated with decreasing molecule size, suggesting that molecular sieving limited adsorption. However, in repeated adsorption tests, where competition between HOCs was more likely to occur, adsorbed pollutant loads exhibited strong positive correlation with log K_{ow}. Sewage sludge as a carbon source for activated carbon has great potential as a sustainable alternative for sludge waste management practices and production of a high-capacity adsorption material.

Keywords: adsorption, organic contaminants, sludge-based activated carbon, stormwater management

1. Introduction

Municipal and industrial wastewater treatment plants produce large volumes of sludges, for which the processing and disposal are becoming complex problems. In Canada, a country with 24 million of its 35 million people connected to municipal sanitary sewers, an estimated 860,000 tonnes of dry biosolids are produced annually (LeBlanc *et al.* 2008). Corresponding numbers for the European Union, with 360 million inhabitants, are approximately 10 million tonnes of produced sewage sludges, a number deemed to be underestimated (Milieu Ltd 2010). Major disposal routes of sewage sludge include incineration, landfilling and application to land (Fytili and Zabaniotou 2008, LeBlanc *et al.* 2008). Incineration faces high capital costs and public concern over air emission risks, while rising land prices and strategies to ban dumping of organic materials have constrained landfilling. Recycling or further use of the sludge is the preferred and sustainable management option. Sewage sludge contains valuable organic matter and nutrients and could be used as a renewable source of fertilizers. Wastewater streams are, however, contaminated with chemicals and by-products from industry – including metals, polychlorinated biphenyls (PCBs); polycyclic aromatic hydrocarbons (PAHs); dioxins and furans – as well as compounds found in common household products – e.g. metals, flame retardants including polybrominated diphenyl ethers (PBDEs); plasticizers such as phthalates; surfactants including alkylphenols; personal care products and pharmaceuticals – which risk being enriched in sewage sludge (Bright and Healey 2003, Harrison *et al.* 2006). The occurrence of contaminants in sludge has led to negative public perception about biosolids and is currently a major deterrent to agricultural application of sewage sludges in many countries (LeBlanc *et al.* 2008).

Since sewage sludge is a carbon-rich, renewable and vast resource which can be obtained at low cost, an alternative use of sludge is for the production of activated carbon (AC) adsorbents, used to remove a wide range of contaminants from air and water. Sludge has been shown to produce high-quality carbons for adsorption of impurities in water, including metals, phenols and dyes (Smith *et al.* 2009, Xu *et al.* 2015). Producing AC from sludge has the potential to be a cost-effective alternative with respect to both waste management and production of low-cost adsorbents. In fact, production costs of sludge-based carbon, which depend on factors such as sludge availability and required processing, including energy costs for pyrolysis and drying, have the potential to be on par with, or even lower than, production costs of commercial ACs (Xu *et al.* 2015).

The pure AC carbon structure is non-polar and accordingly, ACs have shown high adsorption capacity for many types of non-polar or slightly polar organic compounds, including phenolic compounds (Liu *et al.*

2010), pesticides, PCBs (Sotelo *et al.* 2002), phthalates (Venkata Mohan *et al.* 2007), and PAHs (Valderrama *et al.* 2008). The hydrophilicity of ACs can be increased by the presence of polar surface functional groups, and the surface chemistry can be modified to enhance selectivity of specific chemicals. Inorganics, including for example Cu, Pb and Zn (Rivera-Utrilla *et al.* 2011), nitrate, nitrite and ammonia (Afkhami *et al.* 2007, Huang *et al.* 2008), as well as sulfides, chlorides and cyanides (Bansal and Goyal 2005), have been shown to adsorb onto modified ACs.

Activated carbon is regularly used in drinking water and wastewater treatment, but currently has limited application for other types of contaminated water, including stormwater, which is often contaminated with metals, organic pollutants and nutrients. Recent research shows that many persistent organic pollutants, including PAHs, PCBs, PBDEs, phthalates and alkylphenols, are ubiquitous in stormwater (Björklund *et al.* 2009, Björklund *et al.* 2011, Bressy *et al.* 2012, Zgheib *et al.* 2011). Stormwater contaminated with organic substances may pose a threat to receiving waters, as many organic compounds have been shown to persist in the environment, bioaccumulate in organisms, and exhibit adverse effects on human and animal health. To achieve established water quality objectives, stormwater treatment is considered critical.

Contrary to what has been assumed previously, recent studies show that many theoretically hydrophobic organic compounds (HOCs) with high water-octanol partition coefficient (K_{ow}), such as PAHs and phthalates, are found in considerable amounts in the dissolved (<0.7 µm) and colloidal phases of stormwater (Kalmykova *et al.* 2013, Zgheib *et al.* 2011). Consequently, stormwater treatment methods, such as filtration and sedimentation, are assumed to be inefficient for HOCs in non-particulate phases. Adsorption filters have the potential to physically retain suspended pollutants, as well as attracting and chemically attaching dissolved pollutants onto adsorbent surfaces. Adsorption can be adopted in stormwater treatment methods such as storm drain filters and bioretention. Provided that effective media are used, adsorption can be an economical and easily-operated treatment method. Hence, AC produced from sewage sludge has the potential to become a sustainable solution for improving stormwater and receiving water quality.

The objectives of this study were to i) investigate the adsorption of organic stormwater contaminants onto sludge-based carbon in the absence and presence of competing adsorbates; ii) compare the adsorption capacity of sludge-based activated carbon (SBAC) with a surface-modified SBAC and two commercially available ACs. This is the first evaluation of the adsorption efficiency of SBAC for HOCs; adsorption is investigated in batch tests using ultrapure water spiked with organic compounds. Organic contaminants receive particular attention, as there are currently few data on the use of adsorption to remove them from stormwater. Selected organic compounds – four PAHs (fluorene, anthracene, pyrene and benzo[e]pyrene), two phthalates (dibutyl and di(2-ethylhexyl) phthalate), as well as two alkylphenols (4-*t*-octyl- and 4-nonylphenol) – were chosen according to reported stormwater detection frequency (Björklund *et al.* 2011, Bressy *et al.* 2012, Zgheib *et al.* 2012, Zgheib *et al.* 2011) and contrasting characteristics such as hydrophobicity and functional groups (Table S1, Supplementary Material).

2. Material and Methods

2.1. Production of Sludge-Based Activated Carbon

The preparation of SBAC has been described in detail elsewhere (Gong 2013), and is only summarized here. Sludge was collected from the aerobic zone of the wastewater treatment pilot plant at the University of British Columbia, Vancouver, which receives domestic wastewater from the campus. The sludge was centrifuged, dried (105°C) and ground to a fine powder. The powdered sludge was soaked in 5M $ZnCl_2$ for 24 h, dried for 24 h, then pyrolysed at T_{final}=500°C in an electric furnace. After conversion, the SBAC was ground to a powder, washed with 5M HCl followed by distilled water, dried and stored in amber glass bottles.

Physical and chemical characterization of the produced carbon materials included carbon content, BET surface area, pH, cation exchange capacity (CEC), X-Ray Diffraction, and surface functional groups by Fourier transform infrared spectroscopy (FTIR), all explained in detail by Gong (2013).

2.2. Other Sorbents

For comparison, SBAC modified with an oxidizing agent was tested. A pre-study (Gong 2013) showed that impregnating SBAC with 10M HNO_3 (1 g to 10 mL) at 90°C for 4 h produced a modified SBAC (modSBAC) with excellent adsorption capacity for metals, and hence this was tested in this study. Carbonized sludge (CS) was prepared by pyrolysing the sludge using the same method as for the SBAC, but without $ZnCl_2$ impregnation.

Two commercially available ACs from Sigma Aldrich (untreated powder, 100–400 mesh, henceforth referred to as Sigma) and Calgon Carbon (powdered, WPH type for water treatment, 100–325 mesh, henceforth referred to as WPH) were tested in parallel with the carbons produced from sewage sludge.

2.3. Batch Adsorption Tests

2.3.1. Adsorption Isotherms of Organic Compounds

Two solutions were prepared for isotherm tests of HOCs: (1) individual organic compounds spiked at five concentrations (10, 50, 100, 200 and 300 μg/L), and (2) a mixture of all eight compounds, each spiked at the same concentrations range as (1) above. Higher concentrations could not be tested due to the limited water solubility of HOCs. In amber glass bottles, 150 mL ultrapure water was spiked with HOCs, the solution was thoroughly mixed, and 0.015 g of each the four ACs (SBAC, modSBAC, WPH, Sigma) were added. Samples were mixed using an end-over-end rotator at room temperature (20±2°C) for 24 h, then centrifuged at 2000 rpm for 10 minutes: the liquid phase was analyzed for concentrations of HOCs. Samples with individual compounds spiked were prepared in triplicate; all other samples were prepared in duplicate. Blanks of all carbons (SBAC, modSBAC, CS, WPH and Sigma) in water were analyzed to determine leaching of organic compounds and metals.

For each batch of tests, a matrix blank and a matrix spike were prepared following the same procedure as for the adsorption tests to determine contamination and loss of analytes, respectively. Matrix spikes showed acceptable recoveries (>70%) and good precision (<20% RSD) for all compounds. Phthalates are known to cause blank problems since these plasticizers are incorporated in a number of materials found in laboratories (Fankhauser-Noti and Grob 2007). Even though precautions were taken to avoid contamination of samples, DBP and DEHP levels in the matrix blanks varied between <1–3 μg/L and 3–6 μg/L, respectively ($\bar{x}_{\mathrm{DBP}}$=1.5, $\bar{x}_{\mathrm{DEHP}}$=4.8).

To estimate the maximum adsorption of HOCs onto SBAC, adsorption tests were repeated. At the bottom of a glass column (~85 mL), a plug of silanized glass wool was inserted and 50.0 mg SBAC placed on top. Spiked ultrapure water (200 μg/L of each HOCs, all HOCs mixed) was added in batches of 150 mL and passed through the SBAC, with a contact time of approximately 20 min. Collected column eluates were analyzed for remaining HOC concentrations. Prior to the repeated adsorption tests, one batch of ultrapure water and three batches of spiked water were passed through the column and a glass wool plug (no SBAC) to determine contamination and loss of analytes, respectively. Nonylphenol, octylphenol and PAHs were not detected in the blank. DBP and DEHP blank concentrations were ≤0.6 µg/L, i.e. similar to matrix blanks. The recoveries of HOCs were slightly lower after passing through the glass wool, compared to having no glass wool. However, recoveries were not significantly different between matrix spikes and glass wool spikes (independent samples *t*-test, *p*=0.617).

2.3.2. pH Effects on Adsorption

The effect of solution pH on adsorption of HOCs was tested by adjusting the pH of ultrapure water, using 0.1 M NaOH or HCl, to pH = 4, 7 and 9. To 150 mL pH-adjusted water, 0.015 g SBAC was added and the samples were spiked with a mixture of the organic compounds (100 µg/L of each compound). After 24 h mixing, the samples were centrifuged and subsequently extracted.

2.3.3. Kinetics

Prior to the kinetic tests, 0.015 g of the four ACs were soaked in 150 mL Milli-Q water for 24 h, after which the samples were spiked with a mixture of the organic compounds (100 µg/L of each compound). After mixing for 10, 20, 30, 60 and 120 min, the samples were centrifuged and subsequently extracted.

2.4. Reagents, Extraction and Analysis of Organic Compounds

Detailed information on chemicals used for producing SBAC and extracting organic compounds from water are found elsewhere (Björklund and Li 2015, Gong 2013). Water was purified with a Synergy UV Milli-Q system from Millipore. Standards of fluorene (FL), anthracene (ANT), pyrene (PYR), benzo[e]pyrene (BeP), 4-nonlyphenol (NP), dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) were purchased from Sigma-Aldrich, and 4-*t*-octylphenol (OP) from Fluka. 9-chloroanthracene and phenanthrene-d_{10}, from Sigma-Aldrich, were used as internal standards. Stock solutions of the organic compounds, as well as internal and calibration standards of analytes, were prepared in toluene, and working standards for spiking water samples were prepared in acetone. All solutions were stored in amber glass bottles at -18°C. The procedure to extract organic compounds from water and the instrumentation used for analysis are described in detail elsewhere (Björklund and Li 2015) and are summarized in the Supplementary Material.

2.5. Data Analysis

The concentrations of HOCs remaining in the solution after adsorption were used to determine the adsorption capacity (q_e, µg/g). Equations for the adsorption capacity, as well as the Langmuir and

Freundlich isotherm models and the pseudo-first and second order kinetics models, are presented in the Supplementary Material.

IBM SPSS Statistics version 20 software was employed to perform all statistical analyses, such as correlations, *t*-tests and one-way ANOVAs.

3. Results and Discussion

3.1. Characteristics of the Carbon Materials

Characteristics of the sludge-based carbons are presented in detail elsewhere (Gong 2013). In summary, the FTIR spectrum of CS (non-activated) indicated that the absence of chemical treatment led to a lack of functional groups. The differences in intensity of certain bands in the SBAC and modSBAC spectra can be attributed to the oxidation of SBAC with nitric acid, leading to an increase in functional surface groups such as C=O, C-O, C=N, C-N=O, $R\text{-}COO^-$, indicated in the modSBAC spectrum (see Gong [2013] for information on specific peaks).

The yield of SBAC (calculated on ten batches of dry sludge pyrolysis conversion) was approximately 35%, which is comparable to other studies using organic waste products as carbon sources for AC production (Ioannidou and Zabaniotou 2007). The surfaces of SBAC and modSBAC were acidic (**Error! Reference source not found.**); $ZnCl_2$ activation and HCl washing are known to produce acidic ACs (Smith *et al.* 2009). In addition, HNO_3 modification renders the surface even more acidic by introducing oxygen-containing functional groups. The ash content of SBAC (Table 1) was higher than reported content for ACs produced from agricultural wastes, but lower than reported in studies on sludge-based ACs (Ioannidou and Zabaniotou 2007, Xu *et al.* 2015, Yeganeh *et al.* 2006). A low ash content favors surface area and microporosity (Xu *et al.* 2015), hence affecting the adsorption capacity per unit mass. Acid washing, in this case with HCl, decreases the ash content and improves the surface area and porosity of ACs. The SBAC surface area was lower than for tested commercial carbons, but in the range of other reported ACs produced from agricultural waste and conventional carbon sources such as coal, and higher than reported in studies on sludge-based ACs (Ioannidou and Zabaniotou 2007, Smith *et al.* 2009, Xu *et al.* 2015, Yeganeh *et al.* 2006). Modification of the SBAC considerably decreased the surface area (Table 1), possibly due to destruction of the porous structure caused by oxidation with HNO_3 (Yin *et al*. 2007).

Table 1. *Physical and chemical characteristics of raw material and carbonaceous materials.*

Material	Raw material, activation and modification methods	BET surface area [m^2/g]	Ash content [%]	pH ($CaCl_2$ method)	Cation exchange capacity [meq/100 g]
Raw sludge	-	19.8	62.5	6.9	91.1
CS – carbonized sludge	Sewage sludge, not activated	202	39.4	5.3	4.94
SBAC – sewage-based activated carbon	Sewage sludge, chemical activation with $ZnCl_2$	721	9.4	3.4	<1
modSBAC – modified SBAC	Sewage sludge, SBAC modified with HNO_3	86.1	7.4	1.0	n.a.[a]
WPH – commercial AC	Bituminous coal, steam activation	1130	9.9	8.4	126
Sigma – commercial AC	Wood, chemical activation	2110	6.3	8.0	95.3

[a] Not analyzed.

In general, low levels of metals were leached from the ACs (low µg/L levels), except for Zn from SBAC (a residue of the activation agent), corresponding to 6.9 mgZn desorbed per gSBAC, compared to 0.53–1.7 mg/g for the other materials. None of the eight HOCs were detected in the leachate of the four activated carbons.

3.2. Adsorption of Individual and Mixed HOCs onto SBAC

Removal of organic compounds using SBAC was found to be efficient for both individual compounds and a mixture of the eight HOCs. No statistical difference in adsorption capacities (q_e) was detected between samples with individual compounds or a mixture of compounds (independent samples *t*-test, *p*>.05 at all five spike levels). This suggests that competition for adsorption sites on the SBAC was not relevant for the prevailing conditions ($dose_{SBAC}$=0.015 g, 150 mL, ≤300 µg HOCs/L). If all added HOCs were to be completely adsorbed, this would have resulted in a load of approximately 24 mg/gSBAC (i.e. 2.4% of its weight). According to the Product Information for the Sigma Aldrich carbon used in the current study, activated carbon can be expected to adsorb 1–30% ($\bar{x}$≈10%) of its own weight. In this case, it is assumed that adsorption sites on the SBAC surface were still available and that additional adsorption was possible.

Because no statistical difference in adsorption capacity between individual and mixed HOCs was observed, pH effects, kinetic tests, comparisons between different types of ACs, and adsorption isotherms (sections 3.3.–3.6.) were performed on samples containing a mixture of HOCs.

3.3. pH Effects

A one-way ANOVA test reveals that the adsorption capacities of all HOCs were significantly lower for pH = 4 than for a pH of 7 and 9 ($p<0.05$), whereas there was no statistically significant difference between pH 7 and 9. This implies that adsorption of HOCs onto SBAC is near optimal at pH levels normally found in natural stormwater, i.e. slightly above neutral pH (NSQD, 2015).

3.4. Kinetic Tests

The SBAC adsorption capacity fluctuated between 10 and 60 min (Figure 1a). After the initial rapid adsorption phase, where easily available AC surface adsorption sites became occupied, a transition state was reached, most likely giving rise to observed fluctuations in adsorption capacity (Ncibi and Sillanpää 2015). The high-molecular weight compounds needed time to diffuse into smaller and smaller pores and finally reach equilibrium. Similar trends in kinetic data were observed in a previous study on the adsorption of HOCs onto sawdust and pine bark (Björklund and Li 2015).

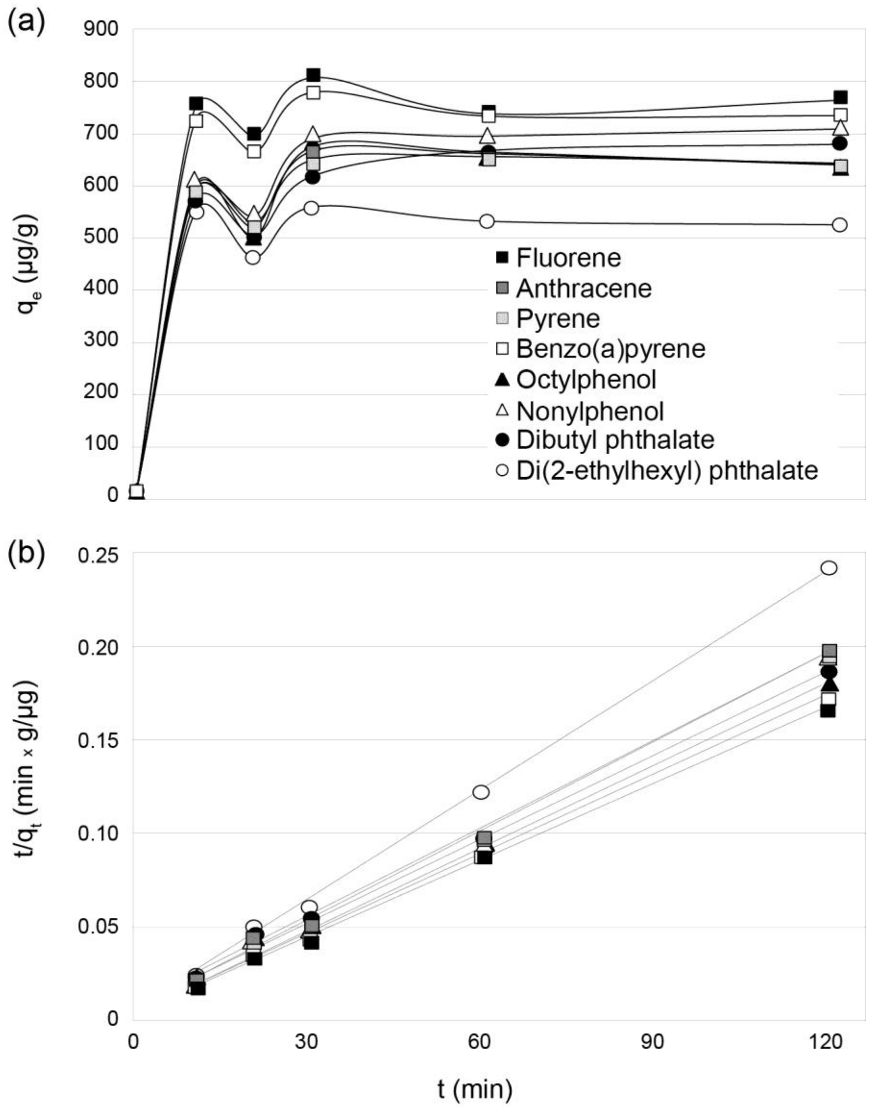

Figure 1. *(a) Capacity (*q_e*) of SBAC to adsorb HOCs at* t*=10–120 min (*$C_{initial}$*=100 µg/L,* $dose_{SBAC}$*=0.015 g); (b) Application of the pseudo-second-order kinetic model to experimental data for adsorption of HOCs onto SBAC.*

Non-parametric Mann-Whitney tests show that the adsorption capacity at 24 h was significantly higher than at 120 min (*z*=-4.79, *p*=.000). At 120 min, q_e:s were indeed higher than at 10 min, though not significantly higher (*z*=-1.66, *p*=.097). Approximately 58–89% of the maximum adsorption (assumed at 24 h) of HOCs was reached within 10 min, compared to 61–91% at 120 min. This implies that most adsorption of HOCs occurred within 10 min contact with SBAC, but that 11–41%, depending on the compound, of the adsorption capacity was only achieved in the following 24 h.

Experimental data did not fit the first-order equation well (Table 2), whereas for the second-order plots R^2≥0.995 for all compounds (Table 2, Figure 1b). However, predicted q_e:s are generally 10–40% lower than experimentally derived adsorption capacities, suggesting moderate agreement between experimental data and the kinetic model. The pseudo-second-order model is based on the assumption that the rate-limiting step is surface adsorption involving chemisorption (Ho and McKay 1999), requiring electron transfer or sharing between surface and adsorbate (Ruthven 2008). Previous studies on the adsorption of PAHs and phthalates onto AC have indicated that both pseudo-first- and second-order models fit experimental data (Abdel daiem *et al.* 2012, Valderrama *et al.* 2008, Venkata Mohan *et al.* 2007).

Table 2. *Coefficient of determination (R^2) for pseudo-first- and second-order kinetic models, as well as intra-particle linear plots for removal of HOCs using SBAC. Fitted parameters of the pseudo-second order model are also presented.*

	First order	**Second order**				**Intrapart. diff.**
	R^2	**R^2**	**q_e[a] [µg/g]**	**q_{exp}[b] [µg/g]**	**k_2[c] [g/(µg·min)]**	**R^2**
FL[d]	0.005	0.999	769	968	$2.11 \cdot 10^{-3}$	0.039
ANT	0.086	0.997	625	942	$1.07 \cdot 10^{-3}$	0.272
PYR	0.161	0.998	625	855	$9.14 \cdot 10^{-4}$	0.336
BeP	0.024	0.999	714	789	$3.92 \cdot 10^{-3}$	0.060
OP	0.342	0.998	667	944	$4.25 \cdot 10^{-4}$	0.570
NP	0.058	0.995	625	932	$9.48 \cdot 10^{-4}$	0.212
DBP	0.538	0.998	667	947	$3.21 \cdot 10^{-4}$	0.656
DEHP	0.014	0.999	500	824	$13.3 \cdot 10^{-2}$	0.002

[a] q_e is the calculated adsorption capacity at t=24 h (assumed equilibrium).

[b] q_{exp} is the experimentally determined q_e at t=24 h.

[c] k_2 is the pseudo-second-order rate constant of adsorption.

[d] FL – fluorene, ANT – anthracene, PYR – pyrene, BeP – benzo[e]pyrene, OP – 4-*tert*-octylphenol, NP – 4-nonylphenol, DBP – dibutyl phthalate, DEHP – di(2-ethylhexyl) *phthalate.*

It can be assumed that the adsorption process follows two consecutive steps: external mass transfer of the adsorbate across the external boundary layer; and intraparticle diffusion within the pores of the adsorbent (Liu *et al.* 2010). To gain insight into the diffusion/transport mechanisms and rate-controlling steps affecting the kinetics of adsorption, experimental results were fitted to Weber's intraparticle diffusion model (Supplementary Material, Eq. 6). If the regression of q_t vs $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step; if not, boundary layer diffusion controls the adsorption to some degree. In this study, none of the HOC plots pass through the origin and R^2:s for the model are moderate to weak (Table 2), likely due to the non-linear trend caused by lower q_t:s observed at t=20 min (Figure 1a). Because of this irregularity in the data, it is difficult to draw conclusions on the sorption process from the shape of the plot, as seen, for example, in the results of Valderrama *et al.* (2008).

3.5. Adsorption of HOCs onto SBAC, modSBAC, WPH and Sigma

The average adsorption capacities of the commercial carbons WPH and Sigma were slightly higher than for SBAC at spike levels of 10–200 µg/L (Table 2). The difference is, however, not statistically significant at the $p<0.05$ level (One-way ANOVA). Capacities for modSBAC were consistently lower than for other tested ACs, but only significantly lower than q_e:s for Sigma at spike concentration 200 µg/L (p=.029) and SBAC at 300 µg/L (p=.018). Adsorption capacities for specific compounds are presented in Figure 3 (SBAC) and Figure S1 (WPH, Sigma and modSBAC). Compared to WPH, which exhibits the highest q_e:s of all tested ACs, the average q_e:s for modSBAC were significantly lower at all spike levels (p=.010–.048). The highest adsorption capacities using modSBAC were found for PAHs, ranging from 2700 to 2970 µg/g at the highest spike level, followed by DBP and DEHP and the alkylphenols NP and OP (1590, 1310, 1250 and 666 µg/g, respectively, Figure S1). Differences in q_e:s between HOCs are, however, not significant at the $p<0.05$ level.

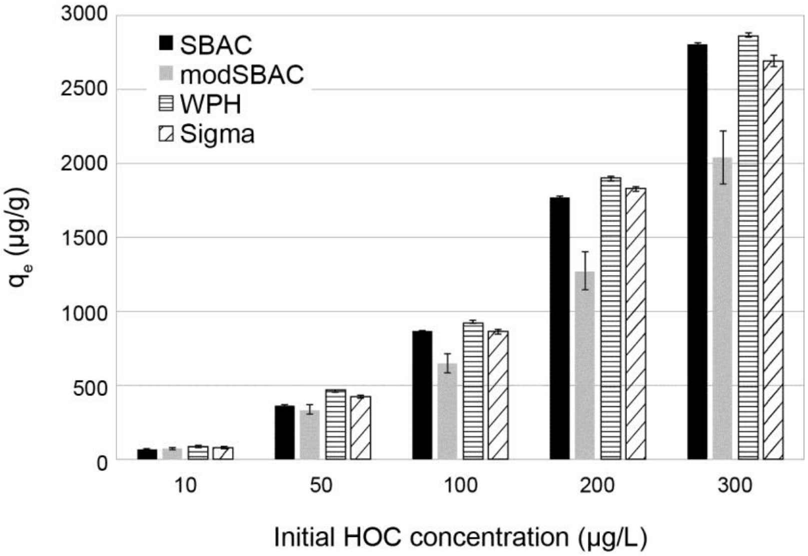

Figure 2. *Adsorption capacity* (q_e) *of HOCs on sewage-based activated carbon (SBAC) and surface-modified SBAC (modSBAC), as well as commercial activated carbons WPH and Sigma. Plotted* q_e*:s are mean of duplicate samples and error bars indicate standard error of* q_e *at each spike level.*

These results indicate that the modified carbon was less effective at adsorbing hydrophobic organic compounds than the other carbons tested. The surface area was greatly reduced when the SBAC was modified (**Error! Reference source not found.**), although porosity is assumed to have a larger effect on adsorption than surface area. Modification is often assumed to negatively affect micro- and meso-porosity of ACs, although studies by Ania *et al*. (2007) and Rivera-Utrilla *et al*. (2011) show that HNO_3-modification does not affect micro-porosity. However, the pore size distribution was not investigated in this study.

The FTIR spectra indicate an increase in oxygen-containing functional surface groups on the modSBAC compared to SBAC (Gong 2013). Several studies have shown that adsorption of both relatively hydrophobic and hydrophilic organic compounds is depressed on polar ACs with surface oxygen groups compared to less polar hydrophobic carbons (Ania *et al.* 2007, Li *et al.* 2002, Moreno-Castilla 2004, Quinlivan *et al.* 2005). On hydrophilic carbons, water molecules are bound to the surface oxygen groups by H-bonds, preventing HOC access to hydrophobic parts of the carbon surface. Aromatic compounds are believed to interact with the carbon surfaces through forces between the π-electrons of the aromatic ring and those present in graphene layers. When the carbon surface is oxidized, electron-acceptor groups, such as carboxylic, are introduced, leading to lower π-electron density in the graphene layers, hence to decreased dispersion interactions. Several studies show that an increase in carboxyl and hydroxyl groups inhibits adsorption of phenolic compounds, both through increased water adsorption and reduced availability of π-electrons (Apul and Karanfil 2015, Smith *et al.* 2009). Oxidation of the modSBAC surface appears to have affected the adsorption of alkylphenols and phthalates more than PAHs. Water adsorption affects all HOCs to the same degree, but because the PAHs contain more aromatic rings than alkylphenols and phthalates, this may lead to increasing strength of π–π interactions (Apul and Karanfil 2015).

3.6. Adsorption Isotherms for HOCs onto SBAC

In general, adsorption capacities ranged from 70 µg/g ($C_{initial}$=10 µg/L) to 2800 µg/g ($C_{initial}$=300 µg/L) for each of the HOCs (Figure 3). This can be compared to a similar study of HOC adsorption onto wood-based products, where adsorption capacities ranged from 0.5–1.3 µg/g ($C_{initial}$=10 µg/L) to 38–45 µg/g ($C_{initial}$=300 µg/L) (Björklund and Li 2015). The highest remaining concentrations (C_e) after 24 h of adsorption were found for DEHP (≤205 µg/L), followed by benzo[e]pyrene (≤72.5 µg/L). The formation of benzo[e]pyrene and DEHP, and to a lesser degree pyrene, colloidal dispersions or emulsions in water was possibly due to their limited water solubility (Table S1); hence benzo[e]pyrene and DEHP adsorption isotherms may be affected (Julinová and Slavík 2012). Linearity of the isotherms (not shown) indicates that saturation was not reached for any HOC. The Freundlich model fits experimental data for some of the HOCs, whereas the Langmuir model exhibits a stronger fit ($R^2 \geq 0.947$) for all compounds tested (Table 3). However, negative q_{max}-values indicate that the Langmuir model cannot adequately explain the adsorption process. The Langmuir model assumes that adsorbed molecules form a monolayer, and it is argued that it describes chemisorption of molecules, also indicated by the pseudo-second order kinetic model. However, both physisorption and chemisorption can occur simultaneously, and experimental results do not always indicate clearly which type of adsorption is predominant. In fact, it has been suggested that the Langmuir isotherm model is not limited to chemisorption, but that a good fit to the model indicates monolayer adsorption, while adsorbent-adsorbate interactions characterized by non-covalent forces such as van der Waals, hydrophobic and electrostatic interactions are possible (Alkaram *et al.* 2009, Valderrama *et al.* 2008). Given the weak fit of the Freundlich model and the negative q_{max}-values of the Langmuir models, we cannot use the models to draw any conclusions on the determinant factor in the adsorption of the organic compounds.

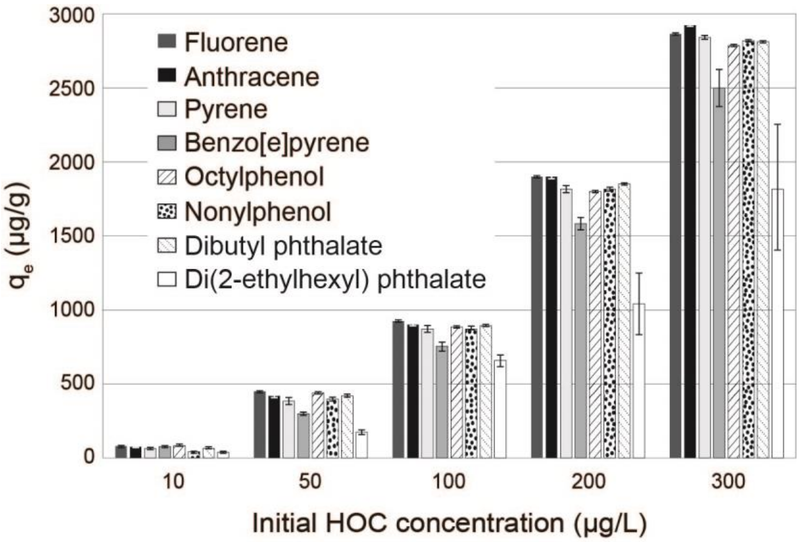

Figure 3. *Adsorption capacity (*q_e*) of HOCs using SBAC at* $C_{initial}$*=10–300 µg/L. Plotted* q_e*:s are mean of duplicate samples and error bars indicate standard error of* q_e*.*

Table 3. ***Coefficient*** *of determination (R^2) and Freundlich and Langmuir isotherm parameters for adsorption of HOCs onto SBAC.*

	Freundlich			**Langmuir**		
	R^2	n[a] [-]	K_F[a] $[(\mu g/g)\cdot(L/\mu g)^{(1/n)}]$	R^2	q_{max}[b] $[\mu g/g]$	K_L[c] $[L/\mu g]$
FL[d]	0.993	0.563	4.24	0.993	-500	-0.081
ANT	0.584	0.588	3.89	0.947	-370	-0.072
PYR	0.740	0.617	2.45	0.971	-588	-0.027
BeP	0.762	0.837	4.45	0.961	$-1.00\cdot10^4$	-0.004
OP	0.987	0.802	5.19	1.000	$-2.00\cdot10^3$	-0.026
NP	0.917	0.339	0.54	0.987	-108	-0.051
DBP	0.970	0.471	1.91	0.982	-270	-0.057
DEHP	0.770	0.517	1.12	0.967	-208	-0.026

[a] K_F and n are Freundlich model constants.

[b] q_{max} is the maximum adsorption capacity.

[c] K_L is the Langmuir constant.

[d] FL – fluorene, ANT – anthracene, PYR – pyrene, BeP – benzo[e]pyrene, OP – 4-*tert*-octylphenol, NP – 4-nonylphenol, DBP – dibutyl phthalate, DEHP – di(2-ethylhexyl) *phthalate.*

The highest adsorption capacities were observed for fluorene, followed by anthracene, DBP and octylphenol (Figure 3). In general, the compounds with higher molecular weight and log K_{ow} exhibited lower adsorption capacities than lower molecular weight congeners of the same compound group. The most hydrophobic compound, DEHP (log K_{ow} 7.7), was adsorbed to the lowest degree of all HOCs tested. The adsorption capacities of HOCs are negatively correlated to log K_{ow} at $C_{initial}$=10–200 µg/L (Spearman's ρ=-0.683 to -0.802). Several studies have failed to find a strong relationship between removal of organic compounds using AC and the compounds' K_{ow}, whereas other studies claim that adsorption of hydrophobic pollutants is driven mainly by hydrophobic partitioning (Bansal and Goyal 2005, Delgado *et al.* 2012, Valderrama *et al.* 2008). Log K_{ow} does not appear to be a good indicator when hydrophobic partitioning is less relevant, for example when removing adsorbates that are polar, protonated/dissociated at solution pH, or small in size. No apparent difference in q_e:s was observed between compound groups, but rather within the three compound groups, and the only apparent trend is lower q_e:s with increasing molecular size, suggesting that SBAC exhibit a degree of molecular sieving for the larger HOCs. Hydrophobic affinity cannot overcome steric hindrance, which has been observed in several studies using microporous ACs (Apul and Karanfil 2015, Delgado *et al.* 2012, Yuan *et al.* 2010).

Competition among HOCs for adsorption sites on the SBAC surface is assumed to be limited at the concentrations tested. As pointed out by Yuan *et al*. (2010), the relationship between adsorption capacity and molecular size may not be straightforward when competitive adsorption arises. Indeed, after 50 batches of repeated adsorption, the less hydrophobic compounds fluorene, octylphenol, nonylphenol and DBP reached at least 50% breakthrough (i.e. remaining concentration in eluate >100 µg/L), whereas the more hydrophobic anthracene, pyrene and DEHP were found at eluate concentrations <70 µg/L. Note that benzo[e]pyrene was not included in the test due to analytical difficulties. The total adsorbed load of each HOC, ranging from 430 (octylphenol and DBP) to 780 µg (DEHP), exhibits a strong relationship with compound log K_{ow} (ρ=0.883, p=0.008).

These results indicate that when competition for adsorption sites becomes a factor, hydrophobicity plays a more important role in the adsorption process. In total, approximately 4.25 mg HOCs were adsorbed to the SBAC, corresponding to 85 mg/gSBAC, or 8.5% of its own weight. This is theoretically not the maximum adsorption capacity of SBAC, as none of the HOCs reached 100% breakthrough in the repeated adsorption tests. Hence, it can be concluded that SBAC is as efficient as many commercial ACs, which can adsorb approximately 10% of their own weight, according to Sigma Aldrich.

In addition to HOCs, natural organic matter (NOM), such as humic and fulvic acids, compete with organic compounds for adsorption sites on AC (Quinlivan *et al.* 2005). The NOM may also block the entrance of smaller pores, leading to reduced adsorption of HOCs. Furthermore, NOM has previously been shown to affect the solubility, hence the adsorptivity, of metals and organic compounds in water (Kalmykova *et al.* 2014, Kalmykova *et al.* 2010). Hence, it is suggested that further studies on the use of SBAC take into consideration the effects of NOM and other competing compounds present in contaminated waters.

3.7. Production and Application of SBAC

Sewage sludge as a carbon source for AC has great potential as a sustainable alternative for sludge waste management practices and production of a high-capacity adsorption material. However, harvesting nutrients without risking side-effects of xenobiotic compounds present in the sludge requires further research to take full advantage of the benefits of sewage sludges. Activated carbons exhibit superior adsorption capacity of organic pollutants compared to many other sorbents used for water treatment (Björklund and Li 2015, Boving and Zhang 2004, Nkansah et al. 2012). Commonly used adsorbents, including zeolite, peat, fly ash, red mud and clays, usually cost less than 0.2 US $/kg, whereas commercial activated carbons normally cost more than 2.0 US $/kg (Xu *et al*. 2015). The costs of producing SBAC, which depend on factors such as sludge availability and required processing, including energy costs for pyrolysis and drying, have the potential to be on par with, or even lower than, those for the production of commercial activated carbon. Studies show that carbons polluted with both metals and organic pollutants may go through several regeneration cycles – using thermal, chemical or stream processes – before the adsorption capacity is considerably decreased (Liu *et al*. 2014, Xu *et al*. 2015). This implies that regeneration may keep costs down and extend lifetime of the material before final destruction through incineration.

Cost-effective production of ACs may lead to broader application of the adsorbent, for example runoff from areas of high traffic count which are often polluted with alarming levels of PAHs and other petroleum-derived hydrocarbons, phthalates, PCBs, etc. (Birch *et al.* 2011, Zgheib *et al.* 2012). Treatment of highly-contaminated stormwater may require considerable pollutant removal to achieve water quality standards before release into receiving waters. Adsorption filters with SBAC could be used as a complementary step after primary treatment of stormwater, e.g. in settling ponds where colloidal and dissolved pollutants are not removed. Activated carbon is regularly used to treat leachates from landfills (Foo and Hameed 2009, Renou *et al.* 2008), often contaminated with metals and persistent organic pollutants, including PAHs, phthalates, dioxins and furans, flame-retardants and pesticides (Eggen *et al.* 2010, Öman and Junestedt 2008). In a previous study on the removal of dissolved, colloidal and particulate HOCs from landfill leachate, (commercial) AC was proven to be efficient in removing all phases of unwanted organic pollutants (Kalmykova *et al.* 2014).

4. Conclusions

Sludge-based activated carbon was easily produced following a straightforward procedure, requiring only a high-temperature furnace and no high-cost specialty chemicals. The resulting SBAC had relatively low ash content (10%), high surface area (700 m^2/g), and low abundance of functional surface groups. Batch adsorption tests indicated low competition between HOCs for adsorption sites, whereas repeated adsorption tests revealed that more hydrophobic compounds were favoured for adsorption. Both batch and repeated adsorption tests suggest that SBAC is as efficient at removing HOCs as many commercial ACs. Before SBAC is applied in filters for stormwater treatment, adsorption in continuous flow systems using natural stormwater with NOM and other present pollutants, including metals and organic pollutants, should be tested. Other pollutants and NOM may negatively affect the adsorption of HOCs by competitive adsorption and/or enhanced HOC solubility.

Using sewage sludge to produce AC has great potential, given the concerns regarding sustainable and cost-effective disposal of sludges, and the fact that the SBAC exhibits adsorption capacities for HOCs comparable to commercially available ACs produced from fossil fuels.

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