Evaluation of low-cost materials for sorption of hydrophobic organic pollutants in stormwater

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ABSTRACT

Conventional stormwater treatment techniques such as sedimentation and filtration are inefficient for removing the dissolved and colloidal phases of hydrophobic organic compounds (HOCs) present in stormwater. Adsorption could be a promising technique for removing colloidal and dissolved pollutants. Five low-cost sorbent materials were investigated in this project, including two minerals – vermiculite and perlite – and three waste products – two pine barks and a sawdust – as potential adsorbents for removal of polycyclic aromatic hydrocarbons (PAHs), alkylphenols and phthalates; HOCs commonly found in stormwater. Adsorption capacity and kinetics were studied through batch adsorption tests using synthetic stormwater spiked with a mixture of HOCs. Vermiculite and perlite exhibited insignificant removal of the organic contaminants. The three wood-based materials retained >80% of the initial HOC concentration (10–250 µg/L). The two barks exhibited slightly higher adsorption capacities of HOCs than the sawdust. For all compounds tested, maximum adsorption onto the wood-based media was reached in <10 min. The highest adsorption capacity was found for PAHs (up to 45 µg/g), followed by alkylphenols and phthalates. No correlation was found between adsorption capacity and physical-chemical parameters such as solubility and partition coefficients (log K_{ow}). Agreement between empirical data and the Langmuir isotherm model, as well as the pseudo-second order kinetic model, suggest chemisorption of HOCs onto a monolayer on wood-based media. This could lead to early saturation of the materials and should be investigated in future studies through repeated adsorption of HOCs, for example in column studies.

KEYWORDS

Adsorption filter; alkylphenols; PAHs; phthalates; pine bark; stormwater management

HIGHLIGHTS

- Adsorbing media can remove colloidal and dissolved pollutants from stormwater.

- Hydrophobic organic compounds compete with dissolved organic matter.

- Wood-based materials exhibit prompt and efficient removal of organic compounds.

- Low-cost filter materials can provide stormwater quality management.

HIGHLIGHTS

1. INTRODUCTION

Recent studies have shown that many organic contaminants are found in urban runoff at levels that exceed national and international water quality standards (Björklund *et al.* 2009, Björklund *et al.* 2011, Bressy *et al.* 2012, Zgheib *et al.* 2012, Zgheib *et al.* 2011). The most frequently detected organic pollutants in urban runoff include polycyclic aromatic hydrocarbons (PAHs) – emitted by combustion and petroleum sources (Howsam and Jones 1998); phthalates – released mainly from plastics such as PVC, where the compounds are used as plasticizers (Björklund 2010); and alkylphenols – additives in fuels, lubricants, polymers, resins, tire rubber, adhesives etc. (Månsson *et al.* 2008). These organic substances show acute toxic, carcinogenic and/or estrogenic effects on aquatic organisms (Jobling *et al.* 1995, Lyche *et al.* 2009, Neilson 1998). Currently, the greater part of urban stormwater is discharged directly, without treatment, into receiving waters worldwide, posing a threat to water quality and aquatic organisms. Removal of organic contaminants from polluted stormwater is considered essential to meet water quality demands imposed by agreements such as the European Water Framework Directive (European Commission 2000).

In conventional stormwater treatment, it is generally assumed that many organic pollutants are attached to particulates, and thus easily removed through sedimentation or filtration. However, studies by Zgheib *et al.* (2011) and Kalmykova *et al.* (2013, 2014) found that a considerable portion of hydrophobic organic pollutants (HOCs) resides in the dissolved and colloidal phases in stormwater. These non-settleable colloids (usually defined as 1-1000 nm) may act as carriers for organic compounds, increasing their mobility through soil pores or filter materials (Badea *et al.* 2013, Kalmykova *et al.* 2014, Roskam and Comans 2009). It is therefore assumed that conventional stormwater treatment techniques are not efficient for removing dissolved and colloidal organic pollutants. Adsorption filters represent a promising technology to separate particulate, colloidal and dissolved HOCs from stormwater, as has previous been shown for organic pollutants in wastewater (Liu *et al.* 2011, Ray *et al.* 2006). However, knowledge on the applicability of adsorption filters to remove HOCs in stormwater is lacking, as previous research has focused on the adsorption of metals (Genç-Fuhrman *et al.* 2007, Wium-Andersen *et al.* 2012).

Adsorption filters for stormwater could, for example, be implemented in storm drains and catch basins, or as complementary devices at pond outlets. However, cost is a major constraint for applying stormwater treatment facilities and should be kept to a minimum to reduce the risk of the facility not being implemented and/or properly maintained. Low-cost adsorption materials that could be used for

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stormwater treatment should therefore be investigated. For sustainability reasons, the adsorption materials should require minimal resources for extraction and processing and should be reusable or recyclable.

The aim of this research was to identify material(s) which promptly and efficiently adsorb a variety of HOCs frequently detected in stormwater. Five cost-effective and globally available materials – the minerals vermiculite and perlite, two pine barks with different pre-treatment, and a sawdust product – were investigated for removal of HOCs. Vermiculite has previously been used mainly for adsorption of metals (Lee 2012, Malandrino *et al.* 2006). However, it has also been proven to be useful for adsorbing di(2-ethylhexyl) phthalate and humic acids (Wen *et al.* 2013). The capacity of perlite to filter particulates and adsorb metals has previously been studied with promising results (Gironás *et al.* 2008, Sarı *et al.* 2007). Bark and sawdust are waste products from the paper, pulp and lumber industry and have been found to adsorb various organic pollutants to a considerable degree (Ali *et al.* 2012, Boving and Zhang 2004). The minerals may be reused (desorption or to catalyse combustion of organics) and the organic materials recycled (composted or incinerated for energy recovery). The contaminants selected for this study include three PAHs (fluorene, anthracene and pyrene), two phthalates (dibutyl and di(2-ethylhexyl) phthalate), as well as two alkylphenols (octyl- and nonylphenol), which exhibit a variety of physical-chemical properties, e.g. molecular weight, water solubility and polarity. Adsorption capacity and kinetics were studied through batch tests using synthetic stormwater spiked with a mixture of HOCs. The sample composition is a simplification of natural conditions where pollutants co-exist, and dissolved organic matter (DOM) may influence the HOCs' solubility and adsorption (Kalmykova *et al.* 2014, Roskam and Comans 2009). The competition between organic compounds and DOM, as well as the solubility effect of DOM, have not been investigated previously in adsorption studies of organic stormwater pollutants. The results of this study can be used to identify adequate adsorption materials for stormwater quality control.

2. MATERIALS AND METHODS

2.1. Material Characteristics and Sources

- The minerals vermiculite and perlite, both heat-expanded, were provided by Perlite Canada Inc. (Lachine, QC, Canada; www.perlitecanada.com). The expanded vermiculite has the capacity to retain several times its weight in water and is ideal for horticultural applications and as an

absorbent for chemical spills. Expanded perlite can also be used to clean up liquid spills and as a filtration agent in the pharmaceutical, chemical and food industries, as well as for filtration of swimming pools and in water treatment plants.

- Heat-treated pine bark (provided by Rent Dagvatten AB, Göteborg, Sweden) contains no added chemicals. The bark is no longer in production, but has been used to clean up spills, e.g. oil and gasoline.

- Zugol (Zugol AB Svensk Barkindustri, Falun, Sweden; www.zugol.se) is a pine-based product (no pre-treatment) used for remediation of spills of oil, gasoline and other chemicals.

- Ecoprool Blue Ecobark (AB Teknisk Miljöutveckling Sv, Torslanda, Sweden; www.ecobark.com) is a fine sawdust treated with polytetrafluoroethylene (PTFE) and is used primarily for absorption of oil and water.
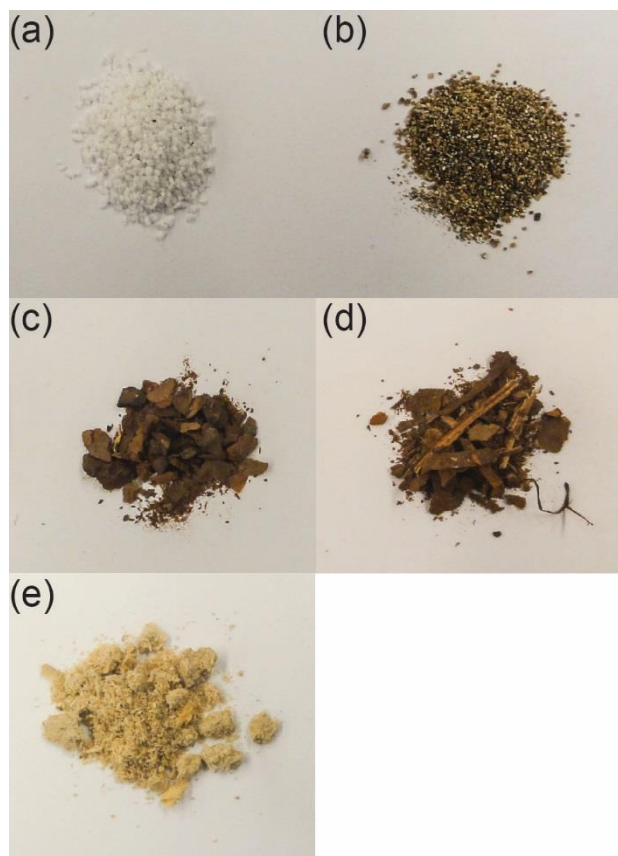
[**Figure 1.** *Sorbent materials used in the adsorption tests, shown before passing through 2 mm sieve: (a) perlite, (b) vermiculite, (c) heat-treated pine bark, (d) Zugol pine bark and (e) Ecoprool sawdust.*]

The sorbents exhibit a great variety of particles sizes, from several centimetres in length down to as small as several microns (Figure 1). To improve the reproducibility of the experiments, the adsorbents were wet-sieved with tap water to the desired particle size (0.6–2 mm), then dried at 105°C overnight before analysis of physicochemical parameters and adsorption testing. The organic contents of the materials were determined by loss-on-ignition (LOI), with the dried media combusted at 550°C. The conductivity and pH were measured on demineralized water, according to Agriculture Canada approved methods (Sheldrick 1984). The specific surface area was determined by the BET nitrogen adsorption method, using a FlowSorb II 2300 surface analyzer (Micromeritics). The characteristics of the adsorbents are summarized in Table 1.

[**Table 1.** *Characteristics of sorbents.*]

Material	Characteristics	BET surface area (m²/g)	Organic matter (%)	pH	Conductivity (µS/m)	Leached DOC[a] (mg/L)	Leached DOC[b], washed (mg/L)
Vermiculite	Expanded	8.6	<1	5.8	9.0	3.6	n/a[c]
Perlite	Expanded	1.2	<1	8.2	6.6	2.3	n/a
Pine bark	Heat-treated	<d.l.[d]	99	4.0	46	290	270
Zugol pine bark	85-90% pine bark, 10-15% wood fibre (pine)	0.56	98	3.5	22	250	170
Ecoprool sawdust	Sawdust 60-100%, 0-1% polytetrafluoro-ethylene	1.4	97	4.3	54	120	85

[a] Dissolved organic carbon; [b] Leached DOC after washing with tap water; [c] Not analyzed; [d] Below detection limit

2.2. Reagents

Water was purified with a Synergy UV Milli-Q system from Millipore. Acetone and dichloromethane (DCM) of high performance liquid chromatography (HPLC) grade were obtained from Fisher Scientific. Toluene (HPLC grade) was obtained from Caledon Laboratories Ltd., while certified ACS grade HCl and NaOH were purchased from Fisher Scientific. Standards of 4-nonlyphenol (NP, 85% content of *para*-isomers), fluorene (FL), anthracene (ANT), pyrene (PYR), dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DEHP), 9-chloroanthracene and phenanthrene-d$_{10}$ (the latter two used as internal standards) were supplied by Sigma-Aldrich. Humic acid (HA) and 4-*t*-octylphenol (OP) standards were purchased from Fluka. Stock

standard solutions of the organic compounds were prepared in toluene and working standards, used to spike the water samples, were prepared in acetone. Internal and calibration standards of analytes were prepared in toluene. All solutions were stored in amber glass bottles at -18°C until use.

2.3. Synthetic Stormwater

The adsorption tests were performed using synthetic stormwater with added DOM, in this case humic acids, and a mixture of organic pollutants. The HA stock solution was prepared by adding approximately 0.5 g of HA standard to 500 mL Milli-Q water, adjusted to pH 10 using NaOH, and placed in a sonication bath for 5–10 min at 40°C to enhance dissolution. The insoluble fraction was removed by filtration through a 0.45 µm cellulose nitrate filter (Millipore). The pH of the filtrate was returned to 7 with 0.1 M HCl before further use. The solution was stored in amber glass bottles at 4°C and monitored frequently for dissolved organic carbon (DOC) stability. The HA stock solution was used for spiking the samples to ~20 mg DOC/L, which is typically found in natural stormwater. A mixture of the seven HOCs was prepared and all HOCs were added in the same amount to samples. No further adjustments of the synthetic stormwater were performed.

2.4. Leaching from Raw Materials

To 50 mL Milli-Q water, 1.0 g of each material was added and mixed for 24 h, passed through a 0.45 µm filter and analyzed for leached DOC using a Lachat Instrument IL 500 TOC analyzer. For the wood-based materials, this was performed on both raw materials and samples washed ten times with tap water (Table 1). For analysis of leached organic compounds from media, 3.0 g of each material was added to 150 mL Milli-Q water and mixed for 24 h before centrifugation and liquid-liquid extraction.

2.5. Adsorption Experiments

Sorption isotherms were determined on samples with 150 mL synthetic stormwater solution (20 mg DOC/L), spiked at five different levels (10–250 µg/L) with the HOC mixture. The HOC concentrations were higher than observed in natural stormwater because of detection limits. After spiking, 1.50 g of sorbent was added to the solution and the samples were mixed for 24 h, using an end-over-end rotator. The samples were then centrifuged at 2000 rpm for 10 min, and those with bark and sawdust were also sieved

through a stainless steel mesh (No. 100); the liquid phase was analyzed for concentrations of organic compounds. The adsorption kinetic test samples were prepared as described above, spiked to 100 μg/L with organic compounds and then mixed for 10, 20, 30, 60 and 120 min. For each series of tests, a matrix blank and a matrix spike were prepared following the same procedure to determine contamination and loss of analytes, respectively. All samples were prepared in duplicate in amber glass bottles and kept at room temperature (20±2°C) during each entire experiment. All glassware was washed with detergents and baked at 550°C for 2 h before use.

2.6.   Extraction and Analysis of Organic Compounds

All organic compounds were simultaneously liquid-liquid extracted using 3×25 mL DCM. The extracts were evaporated to a few mL using a rotary evaporator and then further concentrated to dryness under a stream of N_2. The samples were reconstituted with 1.0 mL toluene before analysis. GC-MS analysis was performed using a 6890 HP/Agilent GC system gas chromatograph with a 6890 series injector and a quadrupole 5973 network mass selective detector (Agilent Technologies, Wilmington, USA) and a 30 m × 0.25 mm I.D. DB-5 column (J&W Scientific, Folsom, CA, USA) coated with (5%-phenyl)-methylsiloxane (film thickness 1 μm). The system was operated in electron impact mode (EI 70 eV). The injector port, transfer line and ion source temperatures were set at 295, 310 and 230°C, respectively. The carrier gas was high-purity helium (99.999%) with a flow of 1.2 mL min^{-1}. The oven temperature was programmed as follows: start at 95°C, to 200°C at 12°C min^{-1}, then to 300°C at 15°C min^{-1} (holding time 10 min). Injection was performed in the splitless mode and the solvent delay time was set to 5 min. For peak identification, the MSD was operated in full-scan mode (*m/z* 45–550) and for quantitative determinations, the MSD was operated in time-scheduled selected ion-monitoring (SIM) mode. Compounds were identified using gas chromatographic retention times and mass spectral patterns of at least three ions. Data acquisition and quantification were carried out using MSD ChemStation software from Agilent.

Internal standard (IS) quantification was performed using 9-chloroanthracene and phenanthrene-d$_{10}$, which are not expected to be present in any of the samples. The IS (100 μl, in toluene) was added to all extracts and all calibration solutions before GC-MS analysis. Five-point calibrations curves, prepared each time a new GC-MS batch was run, were constructed for all target compounds over the concentration range of 2.5 to 250 μg/L.

Recoveries of all analytes were between 70 and 95%; the highest recoveries were observed for alkylphenols and the lowest for phthalates. The detection limits (d.l.) of all compounds were ≤1 µg/L and the blank concentrations were all below d.l., except for the phthalates. Even though precautions were made to avoid contamination, DBP and DEHP levels in the matrix blanks varied between <1 to 3 µg/L and 3 to 6 µg/L, respectively ($\bar{x}_{DBP}$ = 1.5, $\bar{x}_{DEHP}$ = 4.8).

2.7.   Data Analysis

The concentrations of HOCs left in solution were used to calculate the percentage retention (R, %) of organic compounds, also called removal efficiency (see e.g. Zhou *et al*. 2012); and the amount of organic compounds retained by the sorbent, also called adsorption capacity, at equilibrium (q_e, µg/g) and at time t (q_t) (see e.g. Genç-Fuhrman *et al.* 2007, Jang *et al.* 2005). The equilibrium relationship is described by isotherms, here evaluated by linearized forms of both the Freundlich and the Langmuir models (see (Hameed *et al.* 2008, Jang *et al.* 2005). Linearized forms of the pseudo-first-order and the pseudo-second-order adsorption rate equation (see Bulut and Tez 2007, Gök *et al.* 2008) were used to evaluate the adsorption rate from the kinetics tests. To elucidate the appropriate adsorption mechanism, the experimental kinetic results were fitted to the intraparticle diffusion model (Gök *et al.* 2008, Hameed *et al.* 2008).

IBM SPSS Statistics version 20 software was employed to perform all statistical analyses, such as correlations, independent samples *t*-test and One-way ANOVA.

3. RESULTS AND DISCUSSION

3.1.   Leaching from Raw Materials

None of the seven selected HOCs leached in detectable amounts from the materials tested. However, the GC-MS analysis indicated that phenol was leached (not quantified) from both pine bark-based media and the sawdust. Measurements of DOC (Table 1) revealed that the wood-based media leached DOC between ~100 (Ecoprool sawdust) and ~300 mg/L (Zugol pine bark). Other studies have shown that discoloration of pine bark leachate may be attributed to phenols and organic acids, e.g. cellulose, lignin and proteins,

produced during bacterial decomposition of bark polymers (Genç-Fuhrman *et al.* 2008, Ribé *et al.* 2009). Genç-Fuhrman *et al.* (2007) suggested that pine bark is unsuitable for adsorption of metals in stormwater because of the possible transportation of metals with organic acids. This was also studied by others, e.g. Kalmykova *et al.* (2010) and Khokhotova *et al.* (2010). However, Kalmykova *et al.* (2010) showed that even though DOC leaching from peat correlated significantly with metal concentrations in the column effluent in the initial stage of the experiment, leaching of both metals and DOC decreased within a short period of time. Similarly to the Kalmykova studies, lower levels of DOC were leached from the wood-based media after washing (Table 1). This suggests that after initial washing of the pine bark and sawdust, co-solution of pollutants and DOC ceases or slows down.

3.2.   Adsorption onto Perlite and Vermiculite

In tests with vermiculite and perlite, between 10% and 30% retention of the HOCs was observed. However, this retention was not significantly different from analyte losses occurring during extraction and analysis (independent samples *t*-test, $p_{vermiculite}=.237$, $p_{perlite}=.584$). The surfaces of the minerals are negatively charged and may remove ions in polluted water through ionic exchange; hence direct adsorption of neutral HOCs to minerals is expected to be limited. Instead, the removal of HOCs from the water phase is expected to be due to sorption of HOC–HA complexes onto the minerals. Humic acids possess a variety of functional groups that can act as binding sites for both metals and organic compounds (Daifullah *et al.* 2004, Tsang 2014). The most important binding sites are usually oxygen-containing carboxylic and phenolic groups, with pK_a values of ~3 and 9, respectively. Thus, HAs are expected to be negatively charged at the prevailing pH (Table 1), and at pH in natural stormwater (close to neutral pH). Because of the negative charges on both HA and mineral surfaces, removal of HOC–HA complexes from the water phase is limited. However, vermiculite could be modified, e.g. with quaternary ammonium cations, to increase the hydrophobic nature of its surface, consequently enhancing the mineral's affinity to HOCs (Froehner *et al.* 2009, Plachá *et al.* 2008). The minerals are believed to be suitable for metal adsorption (Lee 2012, Sarı *et al.* 2007).

3.3. Adsorption onto Wood-based Sorbents

### 3.3.1. Removal and Adsorption Capacities

The average retention of HOCs exhibited similar trends for the two barks (Figure 2). In general, only 5–20% of the initial HOC concentrations remain in the solution after 24 h of adsorption, with the exception of DEHP. Ecoprool sawdust showed slightly lower removal of NP and DBP, but higher removal of DEHP compared with the two barks. It is apparent from Figure 3, that the adsorption capacities of the two pine barks were very similar, and that the equilibrium concentrations of most HOCs were slightly higher for the Ecoprool sawdust. A consistent adsorption trend cannot be distinguished for ANT, even though the equilibrium concentrations were the lowest among the HOCs.
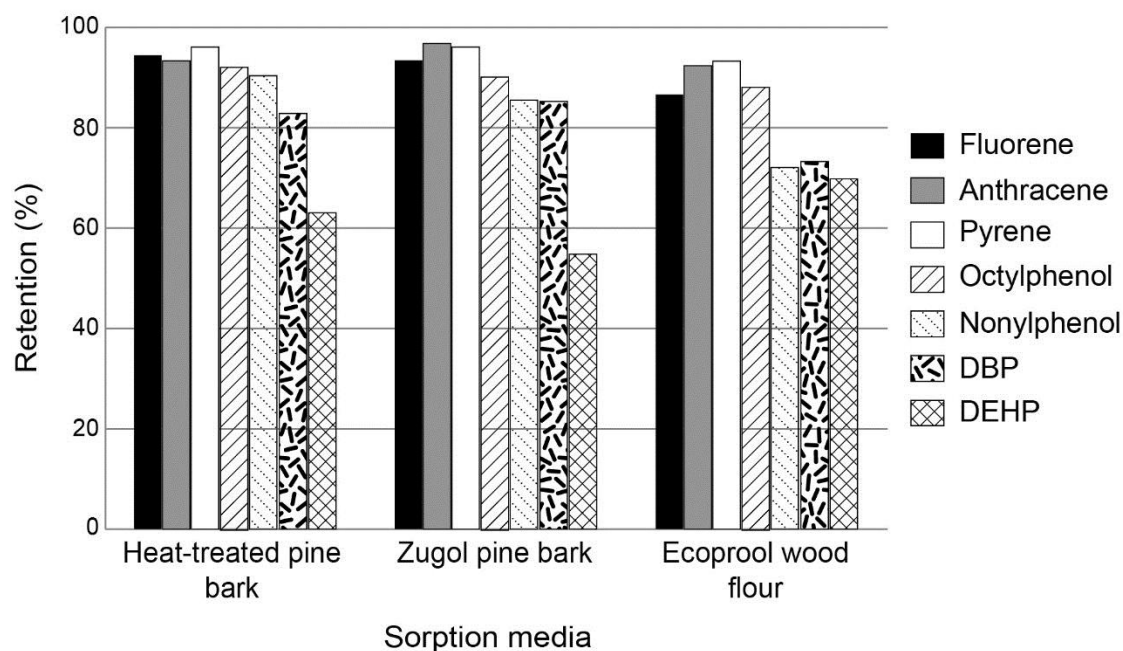
[**Figure 2.** *The mean retention (%) of initial compound concentrations (ranging from 10 to 250 µg/L) using heat-treated pine bark, Zugol pine bark and Ecoprool sawdust as adsorbents. Error bars represent ± one standard deviation around mean computed from five concentration measurements.*]

The adsorption capacities varied from 0.5–1.3 µg/g at the lowest spike concentration tested, up to 38–45 µg/g at the highest concentration (Figure 3). The adsorption capacities did not level out, even at the highest spike concentrations, indicating that the maximum adsorption capacity was never reached. Higher

concentrations could not be tested due to the limited water solubility of the analytes. Averaged over five tested concentrations, the adsorption capacities of the two pine barks followed the same trend: anthracene > pyrene > fluorene > nonylphenol > octylphenol > DBP > DEHP. Adsorption capacities for Ecoprool sawdust followed the order: anthracene > pyrene > octylphenol > fluorene > nonylphenol > DBP > DEHP. In general, all three materials adsorbed PAHs to the highest degree, whereas the lowest adsorption was observed for the phthalates (Figure 3). The phthalates exhibited slightly lower recoveries (~70%) than the alkylphenols (up to 95%) and PAHs (~80%) at the median spike level. We hypothesize that at high spike concentrations the hydrophobic phthalates attached to glassware, and were then lost during extraction and analysis. At lower spike levels, recoveries of DEHP and DBP were indeed higher than at high spike levels. However, corresponding adsorption capacities were still lower than for the other compounds.
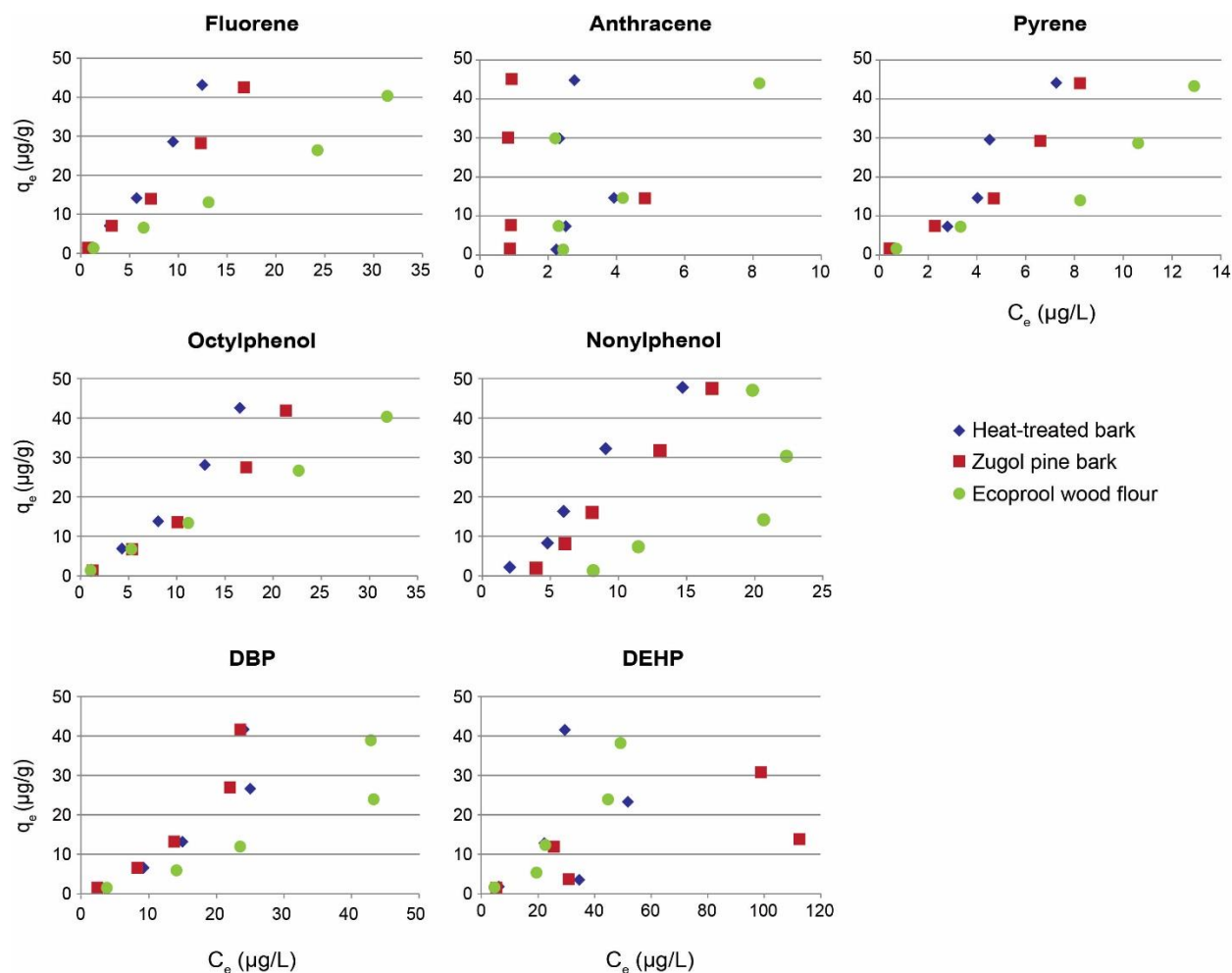
[**Figure 3.** *Adsorption capacities, q_e (µg/g), of (a) fluorene; (b) anthracene; (c) pyrene; (d) octylphenol; (e)*

nonylphenol; (f) dibutyl phthalate; and (g) di(2-ethylhexyl) phthalate as a function of equilibrium concentration, C_e (µg/L) onto heat-treated pine bark, Zugol pine bark and Ecoprool sawdust.]

In a study featuring another type of pine bark and fibres of polyethylene and polypropylene (PP/PE), similar adsorption trends were seen: maximum adsorption capacities ranged from 37 to 42 µg/g, the highest observed for PAHs and the lowest for phthalates (Björklund and Li 2014). Further, similar adsorption capacities (≤12 µg/g, maximum initial concentration 50 µg/L) of FL, ANT and PYR onto aspen wood were reported by Boving and Zhang (2004), whereas Ray *et al*. (2006) found ≤70 µg/g FL and benzyl butyl phthalate adsorbed onto hardwood mulch (maximum initial concentration ~400 µg/L).

It has previously been found, e.g. Liu *et al*. (2014) and Tóth *et al*. (2012), that adsorption of a mixture of compounds may lead to lower adsorption capacities of a specific compound compared to individually adsorbed compounds. The reduction can be attributed to interaction and competitive adsorption between the compounds. However, the current conditions, where HOCs and humic acids co-exist, are expected to be more similar to natural conditions. Hence individual compounds were not tested.

3.3.2. Adsorption Isotherms

For most compounds, satisfactory correlation coefficients were obtained for both the Langmuir and the Freundlich models (Table 2). Better agreement was generally observed for the Langmuir model, except for nonylphenol, although most compounds exhibited negative q_{max}-values, indicating that the Langmuir model cannot adequately explain the adsorption process. In addition, adsorption of anthracene onto all three wood-based media could not be predicted well by either of the models (Table 2).

[**Table 2.** *Correlation coefficients (R^2) and adsorption isotherm parameters for Freundlich and Langmuir linear model plots.*]

	Heat-treated Pine Bark			Zugol Pine Bark			Ecoprool Sawdust		
	Freundlich								
	R^2	n^a	$K_F{}^b$	R^2	n	K_F	R^2	n	K_F
FL[c]	0.997	0.840	1.34	0.996	0.923	1.31	0.997	0.944	0.971
ANT	0.117	0.472	1.11	0.008	6.09	2.84	0.295	0.719	1.36
PYR	0.946	0.765	1.58	0.978	0.896	1.68	0.969	0.899	1.33
OP	0.996	0.809	1.08	0.995	0.845	0.993	0.999	1.03	1.13
NP	0.959	0.472	0.532	0.915	0.370	0.293	0.843	0.228	0.018

	0.983	0.595	0.433	0.988	0.662	0.571	0.983	0.692	0.406
DBP	0.983	0.595	0.433	0.988	0.662	0.571	0.983	0.692	0.406
DEHP	0.550	0.651	0.285	0.799	0.965	0.455	0.963	0.661	0.340

Langmuir									
	R^2	$q_{max}{}^d$	$K_L{}^e$	R^2	q_{max}	K_L	R^2	q_{max}	K_L
FL	0.999	-39.5	-0.047	0.999	-76.9	-0.024	1.000	244	0.004
ANT	0.253	-1.51	-0.284	0.058	29.6	0.196	0.128	-14.2	-0.078
PYR	0.995	-37.3	-0.069	0.999	-294	-0.011	0.999	-137	-0.014
OP	0.999	-31.5	-0.039	0.999	-43.9	-0.024	1.000	200	0.007
NP	0.933	-3.63	-0.107	0.778	-1.95	-0.088	0.765	-0.508	-0.055
DBP	0.989	-7.11	-0.041	0.997	-11.5	-0.037	0.997	-11.0	-0.020
DEHP	0.913	-5.64	-0.017	0.962	-60.2	-0.002	0.995	-10.1	-0.018

[a] n^{-1} adsorption strength (dimensionless); [b] K_F constant related to the adsorption capacity $[(\mu g/g)(L/\mu g)^{1/n}]$; [c] FL – fluorene, ANT – anthracene, PYR – pyrene, OP – octylphenol, NP – 4-nonylphenol, DBP – dibutyl phthalate, DEHP – di(2-ethylhexyl) *phthalate;* [d] K_L constant related to the energy of adsorption (L/μg); [e] q_{max} maximum adsorption capacity (μg/g)

One of the assumptions of the Langmuir model is that each adsorption site can hold only one molecule, resulting in a monolayer coverage (Boparai *et al.* 2011). Because of the monolayer formation, the Langmuir model is said to describe chemisorption better than physisorption (Ruthven 2008). Chemisorption involves short range, strong chemical bonds, e.g. covalent, ionic and metallic bonds, while physisorption is attributed to longer range and weaker van der Waals forces between adsorbate and adsorbent. However, ionic and metallic bonds between the HOCs and wood cells are unlikely. In addition, considering the negative Langmuir q_{max}-values observed for most compounds, and the many possible sorption interactions between the adsorbents and the sorbates, physisorption cannot be ruled out.

3.3.3. Factors Affecting Adsorption

Adsorption behavior depends on the characteristics of the adsorbent, e.g. surface area, surface functional groups and pore sizes; the properties of the adsorbate, such as solubility, partitioning coefficient (log K_{ow}) and molecular size; as well as operational conditions, including pH, temperature and presence of competing adsorbates. The tested organic adsorbents show small surface areas (Table 1) and the organic matter content, related to partitioning (Zhou *et al.* 2012), cannot successfully explain differences in adsorption capacities between adsorbents. In theory, the higher the log K_{ow}, the greater the tendency of organic compounds to adsorb to organic matter. In this study, strong negative relationships between log K_{ow} and average adsorption capacities were found for heat-treated pine bark (Pearson's *r*=-0.91) and Zugol bark (*r*=-0.98), whereas the relationship for Ecoprool sawdust was moderately negative (*r*=-0.67). The

lowest adsorption capacities were generally found for DEHP, which exhibits the highest log K_{ow} (7.7) of all compounds tested. Even if DEHP is excluded from the correlation calculations, the relationship between adsorption capacities and log K_{ow} remain negative for all three materials. Similarly, Liu *et al*. (2014) found the adsorption capacity for three PAHs to be negatively correlated to their log K_{ow}. In addition, Ray *et al*. (2006) were unable to find a correlation between removal capacity and hydrophobicity for a range of organic compounds, including PAHs and phthalates, adsorbed onto hardwood mulch. These results indicate that factors other than hydrophobicity may govern the sorption process in these cases.

The molecular size may affect the adsorption when easily accessible sites on the adsorbent surface are already occupied and only micropores are available. The molecular size may explain why the phthalates (DBP: 0.41×1.45 nm, DEHP: 0.53×1.66 nm [Kiso *et al.* 2001]) are adsorbed to a slightly lower extent than both PAHs (ANT: 0.50×0.92 nm, PYR: 0.68×0.93 [Seitz 2013]) and alkylphenols (NP: 0.68×0.42 nm [Liu *et al.* 2010]). However, as maximum adsorption was never achieved (Figure 3), macropores could still be available, which would mean that molecular size does not affect adsorption to a large degree.

The PAHs are non-polar molecules, while phthalates and alkylphenols contain both hydrophobic hydrocarbon chains and hydrophilic ester and hydroxyl groups, respectively, giving them both polar and non-polar segments. Wood cells contain both non-polar parts, for example fatty acids and methyl groups, and polar oxygen-containing groups, including carboxyl (–COOH), hydroxyl (–OH) and carbonyl (–C=O) groups (Rowell *et al.* 2012). Hence, both polar and non-polar compounds should be able to adsorb onto the wood cell structure. The marginally lower adsorption capacities for alkylphenols and phthalates compared to PAHs may be due to competition from both non-polar and polar molecules at wood cell adsorption sites. In addition, adsorption of alkylphenols may be hindered by the phenol group's strong affinity to water (Kim *et al.* 2011). Although no statistical difference in adsorption capacities between materials was detected (One-way ANOVA: $F(4, 30)=0.327$, p=.858), there was a trend, with lower capacities for the Ecoprool sawdust. This material is treated with ≤1% polytetrafluoroethylene (PTFE), which has a hydrophobic and lipophobic fluorocarbon tail (Lehmler 2005). This treatment renders the material more chemically inert, and may explain the reduced adsorption of HOCs.

3.3.4. Effect of Humic Acids

One of the hypotheses of this study was that humic acids will attract parts of the HOCs through hydrophobic effects, and this will impair HOC adsorption onto organic materials. A previous study showed that humic colloids and attached organic contaminants are not efficiently adsorbed by peat because of the similar surface charge (Kalmykova *et al.* 2014); this could also be expected for wood cells. In addition, as previously discussed, HAs may also occupy adsorption sites, leading to decreased adsorption of HOCs. The difference in adsorption when HAs are present and absent was not investigated in the current study. However, the high removal rates of HOCs (generally 70–95%, Figure 2) suggest that HA did not have a major negative impact on HOC adsorption onto barks and sawdust. The bark and wood leach organic acids which lowers the pH of Milli-Q water to 3.5–4.3 (Table 1). At this pH, parts of the surface groups on HA are expected to be uncharged, and the less hydrophilic parts of the humics may bind HOCs more effectively than at neutral pH (Daifullah *et al.* 2004). However, HA is predominantly negatively charged at the prevailing pH in synthetic stormwater samples (close to neutral, lower dose of material compared to pH tests). Hence adsorption of HA onto the wood-based materials is limited.

According to McCarthy and Jimenez (1985), binding of HOC (in their case the high-molecular weight PAH benzo[a]pyrene) to HAs occurs very quickly, but it is also reversible. Humic acids with greater oxygen content and more functional groups tend to be more hydrophilic and less effective in binding hydrophobic non-ionic organic compounds (Suffet *et al.* 1994). This suggests that the stronger partitioning of HOCs to wood cells than to HA is due to the cells' larger abundance of hydrophobic binding sites. The small variations in adsorption between compounds (Figure 3) could be due to a higher partitioning of the slightly polar alkylphenols and phthalates to polar parts of the humic acids, as opposed to PAHs, which are non-polar. Previous studies, e.g. Landrum *et al*. (1984), Durjava *et al*. (2007) and Sun *et al*. (2008), have reported that humic acids of different origin – for example Aldrich humic acids and natural DOM from ponds and lakes – vary in their structure, and hence exhibit distinctive sorption behaviour of organic contaminants e.g. depending on the contaminants' water solubility. Further studies should test the adsorption behaviour of HOCs using natural stormwater, where naturally occurring DOM may show different sorbent behaviour than the humic acids tested in the current study. In addition, by using natural stormwater, the impact on adsorption of factors such as pollutant concentrations (elevated concentrations were used in this study) and particle content can be evaluated.

3.4.   Adsorption Kinetics

Bulk adsorption of HOCs occurred within 10 min of contact with all three organic materials (Figure 4). Shorter contact times could not be tested for practical reasons. Such relatively fast adsorption has previously been observed for the same HOCs onto another type of pine bark and PP/PE fibres (Björklund and Li 2014), for metals onto mulch (Jang *et al.* 2005), and bisphenol A onto natural sorbents such as rice husk, sawdust and peat (Zhou *et al.* 2012). The differences in retention at 120 min and 24 h (Figure 2) were generally 2–10%, and adsorption capacities at 120 min and 24 h were not statistically different for any of the materials tested (independent samples *t*-test, $p > .05$). In fact, lower DEHP adsorption was observed at 24 h than at 120 min, indicating that DEHP may be released once it has been adsorbed onto the materials tested. As seen in Figure 4, this phenomenon can also be observed at 20 min for the heat-treated pine bark and at 20-30 min for Ecoprool sawdust, where the adsorption was less than at 10 min. The exact reasons for this trend are not known in this study.
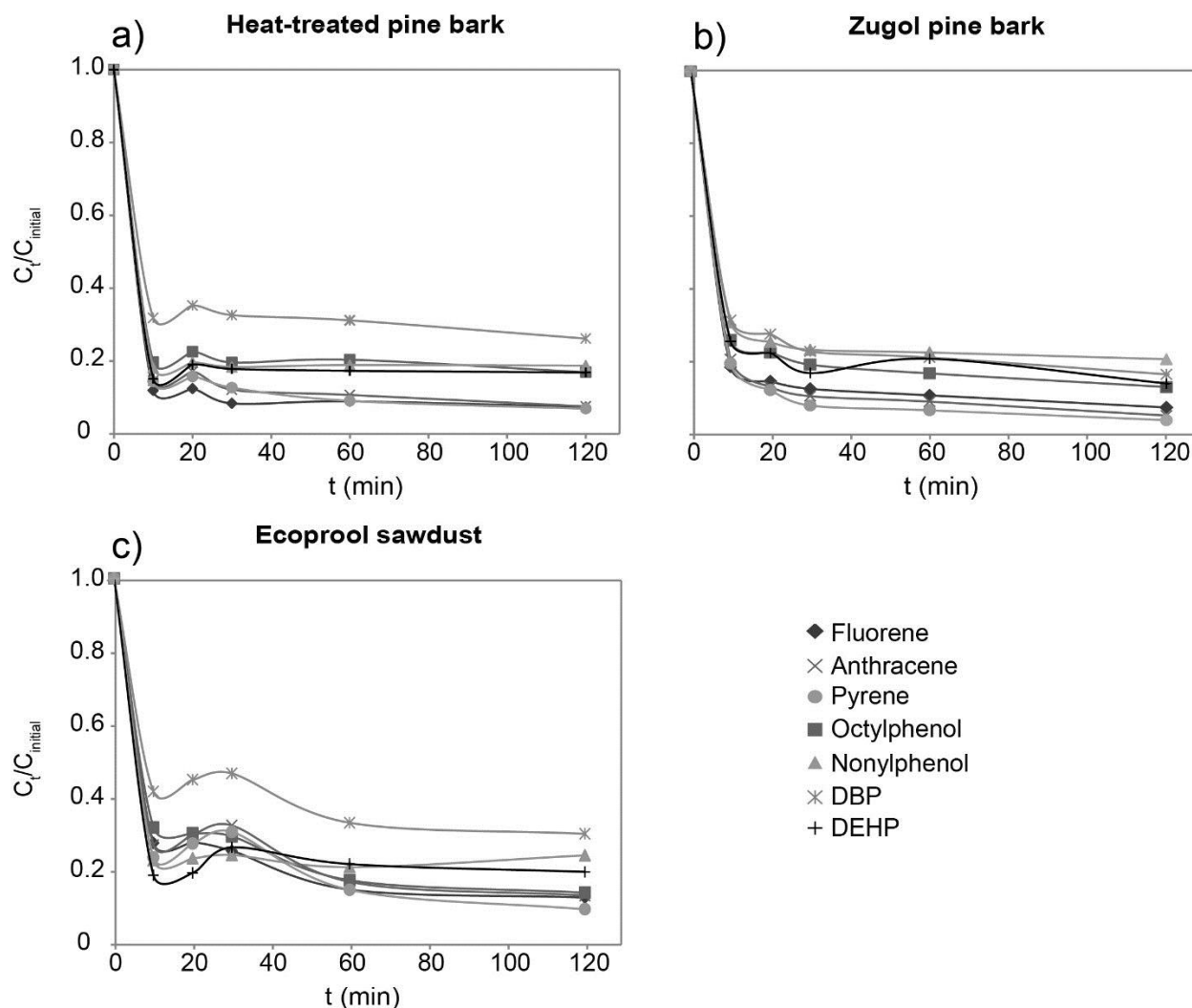
[**Figure 4**. *Fraction of HOC adsorbed ($C_t/C_{initial}$) onto (a) heat-treated pine bark, (b) Zugol pine bark and (c) Ecoprool sawdust as a function of time.*]

The time-dependent adsorption was studied by applying pseudo-first-order and pseudo-second-order equations to empirical data. The plots of the second-order model were found to be linear with good correlation coefficients for all compounds (Table 3). Further, there is good agreement between experimental (q_{exp}) and calculated (q_{calc}) adsorption capacities. Hence, the pseudo-second-order model well represents adsorption kinetics in this study. The kinetics can be used to draw conclusions on controlling reaction pathways, such as chemisorption versus physisorption, and adsorption mechanisms, for example external versus intraparticle diffusion (Boparai *et al.* 2011). Ho and McKay (1999) suggested chemisorption behaviour when the pseudo-second-order model is valid. This is also suggested by the strong correlation with the Langmuir isotherm (Table 2). Formation of a monolayer could lead to early

saturation of the materials and should be investigated in future studies through repeated adsorption of HOCs, for example in column studies. Column studies could also be used to investigate how shorter contact times (<10 min) affect the retention of HOCs.

[**Table 3.** *Correlation coefficients (R^2) for pseudo-first- and second-order, as well as intra-particle linear model plots, and second-order model parameters for adsorption onto heat-treated pine bark, Zugol pine bark and Ecoprool sawdust.*]

	First-order	Second-order				Intra-particle
	R^2	R^2	$k_2{}^a$	$q_{calc}{}^b$	$q_{exp}{}^c$	R^2
Heat-treated Pine bark						
FL[d]	0.738	1.000	0.081	14.0	14.1	0.692
ANT	0.919	1.000	0.036	14.0	14.4	0.808
PYR	0.953	1.000	0.036	14.2	14.4	0.896
OP	0.635	1.000	0.060	12.5	13.8	0.489
NP	0.004	1.000	3.20	12.2	14.1	0.009
DBP	0.836	0.999	0.031	11.2	12.8	0.701
DEHP	n/a[e]	1.000	0.303	12.5	11.7	0.005
Zugol Pine Bark						
FL	0.924	1.000	0.034	14.1	13.9	0.925
ANT	0.820	1.000	0.028	14.5	14.3	0.815
PYR	0.882	1.000	0.031	14.7	14.3	0.769
OP	0.981	1.000	0.027	13.4	13.5	0.943
NP	0.699	1.000	0.051	12.1	13.8	0.742
DBP	0.970	1.000	0.023	12.9	12.9	0.916
DEHP	n/a	0.998	0.031	13.1	11.2	0.680
Ecoprool Sawdust						
FL	0.221	0.999	0.017	13.6	13.0	0.889
ANT	0.851	0.996	0.013	13.6	14.4	0.728
PYR	0.930	0.995	0.011	14.2	13.8	0.698
OP	0.957	0.998	0.014	13.5	13.3	0.917
NP	0.002	0.999	-0.195	11.4	12.1	0.005
DBP	0.846	0.995	0.014	11.0	11.5	0.709
DEHP	n/a	0.999	0.084	12.1	11.7	0.000

[a] k_2 rate constant [g/(µg·min)]; [b] q_{calc} calculated and [c] q_{exp} experimentally derived adsorption capacity (µg/g); [d] FL – fluorene, ANT – anthracene, PYR – pyrene, OP – octylphenol, NP – 4-nonylphenol, DBP – dibutyl phthalate, DEHP – di(2-ethylhexyl) *phthalate;* [e] not applicable, due to $q_e=q_t$ for some time points, its log could not be calculated and plotted.

The mechanism of adsorption from solution is usually divided into two major rate-controlling steps with the adsorbate diffusing (i) from the bulk solution to the external surface of the adsorbent; and (ii) diffusion from the outer surface into the inner pores (Doğan and Alkan 2003, Zhou *et al.* 2012). The external surface sorption is often a faster process due to the large surface area available during the initial stage of the adsorption. As the surficial adsorption sites become occupied, the adsorption rate is controlled by the intraparticle diffusion process. If intraparticle diffusion occurs, a plot of q_t versus $t^{1/2}$ of the intraparticle diffusion model is linear. If the curve passes through the origin, this is the sole rate-limiting step (Gök *et al.* 2008, Hameed *et al.* 2008). In general, the greatest deviation from linearity was observed for the heat-treated pine bark, and the correlation coefficients for the other materials varied considerably between compounds (Table 3). Similar to results presented by Gök *et al*. (2008) and Bulut and Tez (2007), the plots for most compounds' adsorption onto Zugol pine bark initially exhibited a rather steep, linear portion followed by a less steep, linear portion, or a plateau starting at ~30 min in the case of NP and DEHP. Gök *et al*. (2008) and Bulut and Tez (2007) suggested that the initial portion of the curve is attributed to bulk sorption onto macropores on the adsorbent surface; the second part illustrates the intraparticle mesopore and micropore diffusion; and the plateau corresponds to the equilibrium stage. Intraparticle diffusion plots of heat-treated bark and Ecoprool sawdust did not exhibit plateaus for any of the compounds, indicating that equilibrium was never reached. However, by comparing the adsorption capacity at 2 h and 24 h, relevant differences were not detected. This trend is, however, only an indication, as only five time steps were investigated. None of the linear plots passed through the origin, indicating that even though intraparticle diffusion was involved in the process for adsorption of certain compounds onto the three wood-based materials, it was not the sole rate-limiting step (Gök *et al.* 2008, Hameed *et al.* 2008). This suggests that macropores may still be available for adsorption and that equilibrium is not reached. In fact, Figure 3 indicates that maximum adsorption capacity was not reached, even at the highest spike level. Hence adsorption sites are still available.

4. CONCLUSIONS

The capacities of vermiculite, perlite, heat-treated pine bark, Zugol pine bark and Ecoprool sawdust to sorb a mixture of three PAHs, two alkylphenols and two phthalate were investigated by means of batch tests using synthetic stormwater with ~20 mg DOC/L. This approach is closer to natural conditions, where pollutants and DOC co-exist, than testing individual compounds in pure water. This approach can be used

for an initial and relatively fast evaluation of materials e.g. with adsorption filters for stormwater treatment.

A maximum sorption close to 45 µg/g was achieved for the three PAHs onto two tested pine barks (24 h contact, initial concentration of each HOC 250 µg/L, sorbent dose 10 g/L sample solution). Slightly lower sorption capacities were found for alkylphenols and phthalates. This may be explained by steric hindrance (phthalates), competition for sorption sites between polar and non-polar compounds (alkylphenols and phthalates) and different affinity to humic acids. The sorption capacities of Ecoprool sawdust were slightly lower than barks for most compounds tested; possibly due to the sawdust being treated with ≤1% PFTE, which is chemically inert. However, significant differences in adsorption capacities could not be found between compounds or between materials. The results indicate that heat-treated pine bark, Zugol pine bark and Ecoprool sawdust are promising adsorbents for removing HOCs from stormwater. On the other hand, vermiculite and perlite did not significantly remove tested HOCs. Direct adsorption of HOCs on the negatively charged mineral surface is unlikely to occur, and at the prevailing pH (6-9) HOC–HA complexes did not sorb onto the minerals.

The bulk adsorption of all HOCs occurred within 10 min of contact with the wood-based materials. This is promising given that the water retention time in stormwater filters is likely to be of that order. Congruence with the pseudo-second-order model and the Langmuir isotherm model suggests chemisorption of HOCs onto a monolayer, which could lead to early saturation of the sorbents.

5. ACKNOWLEDGEMENTS

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