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Research article

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 (10–300 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 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.

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1. Introduction

Recent studies have shown that many organic contaminants are found in urban runoff at levels exceeding national and international water quality standards (Björklund et al., 2009, 2011; Bressy et al., 2012; Zgheib et al., 2012, 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 lubricants, polymers, 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

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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 focus 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 stormwater treatment should therefore be investigated. For sustainability reasons, the adsorption materials should require minimal resources for extraction and processing and 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). The mineral 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 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 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). 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 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) 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) is a fine sawdust treated with polytetrafluoroethylene (PTFE) and is used primarily for absorption of oil and water.

The sorbents exhibit a great variety of particles sizes, from several centimetres in length down to as small as several microns (Fig. 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), 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). Characteristics of the adsorbents are summarized in Table 1.

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

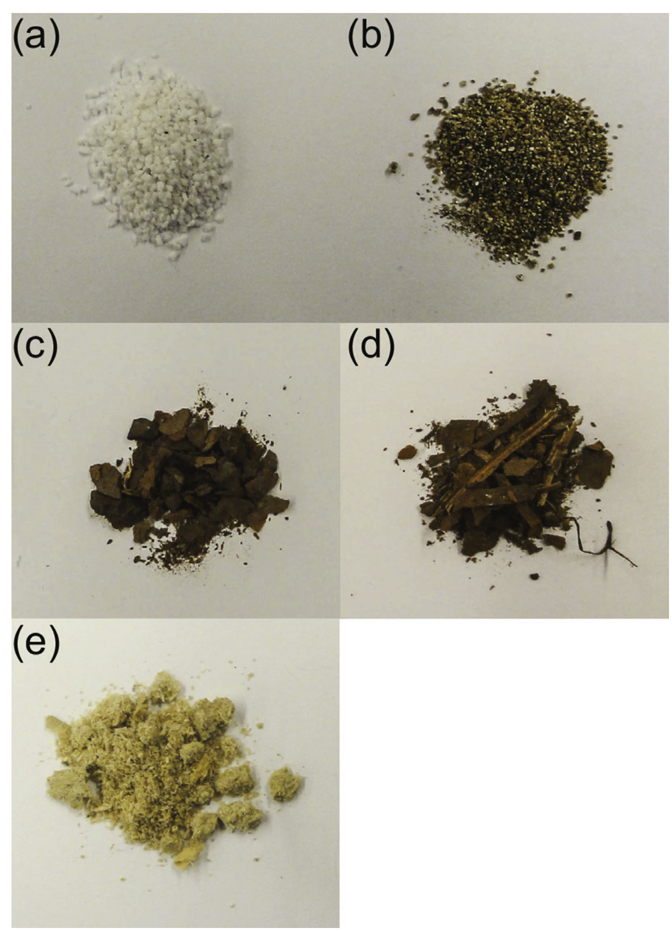

Fig. 1. Sorbent materials used in the adsorption tests, shown before passing through 2 mm sieve: (a) perlite, (b) vermiculite, (c) heat-treated pine bark, (d) Zugol pine bark and (e) Ecoprool sawdust.

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