Removal of hydrocarbons from synthetic road runoff through adsorptive filters
Andreas Vesting, Eva Heinz, Brigitte Helmreich and Marc Wichern

ABSTRACT
Compact filter systems, which are installed to significantly reduce the load of pollutants from road runoff, are very promising treatments for urban runoff. The objective of this research was to evaluate the effectiveness of activated carbon, activated lignite, zero valent iron, exfoliated graphite, amorphous ferric hydroxide, and activated alumina at removing petrol hydrocarbons from synthetic road runoff. Therefore, the kinetics and the equilibrium adsorption of petrol hydrocarbons onto these adsorbents were investigated using column adsorption experiments at levels ranging from 100 to 42 g L⁻¹. Of the tested adsorbents, exfoliated graphite is the most effective with a maximum adsorption capacity for petrol hydrocarbons of 3,850 mg g⁻¹. The experimental equilibrium data are fitted to the Freundlich and Langmuir models.

Key words | best management practice, hydrocarbons, road runoff, sorption, sorption kinetics

INTRODUCTION
Stormwater runoff from traffic areas has been highlighted as a major source of environmental pollution (Davis & Birch 2010; Sablayrolles et al. 2011; Bartlett et al. 2012). It contains a complex matrix of pollutants originating from both the atmosphere and the road surface. Organic pollutants, such as volatile organic compounds (VOC), aliphatic hydrocarbons, and polycyclic aromatic hydrocarbons (PAH), and inorganic pollutants, such as heavy metals, constitute the main contaminants in road runoff (Moilleron et al. 2002; Brown & Peake 2006; Davis & Birch 2010; Helmreich et al. 2010). Owing to increasing knowledge about the pollutant distribution and its environmental transport and the risks posed by stormwater discharge from traffic areas into the environment (Zgheib et al. 2011; Ellis et al. 2012), management of urban runoff pollution has become an increasingly important environmental concern. Recent regulations (e.g., the European Union (EU) Water Framework Directive (European Commission 2000) and the EU Environmental Quality Standard Directive (European Commission 2008) emphasize the importance of stormwater treatment in protecting the quality of receiving bodies of water (Gasperi et al. 2009).

Studies have shown that, by implementing measures to treat polluted runoff, which are often referred to as structural best management practices (BMPs), a significant improvement in stormwater quality can be achieved (Hatt et al. 2009). BMPs can be categorized into four main groups: (a) filter strips and swales, (b) infiltration systems (e.g., soakaways, infiltration trenches and infiltration basins), (c) storage facilities (e.g., retention ponds, lagoons, and constructed wetlands), and (d) alternative road structures (e.g., porous paving and porous asphalt surfaces) (Eriksson et al. 2007). Some of these BMPs retain pollutants insufficiently. Their main purpose is to reduce the urban runoff peak. Therefore, the development of compact decentralized treatment facilities with low space requirements that effectively retain pollutants is necessary (Siriwardene et al. 2007; Helmreich et al. 2010).

Most studies of the treatment of urban runoff using these new decentralized facilities have focused on heavy metal removal (Genc-Fuhrman et al. 2007; Hilliges et al. 2015). Organic trace pollutants have been disregarded so far. Only one recently published paper focused on the removal of methyl tert-butylether (MTBE), a representative VOC, from urban road runoff using activated carbon and activated lignite (Li & Helmreich 2014). Therefore, effective adsorbents that are suitable for use in compact filter systems must be found to treat organic pollutants. While MTBE has been detected in urban runoff in low concentrations (the median value was 1.5 μg L⁻¹) (Borden et al. 2002),
concentrations of petrol hydrocarbons on the mg L\(^{-1}\) scale (the median value was 0.5 mg L\(^{-1}\)) in urban runoff have been found (Moilleron et al. 2002). In contrast to organic trace pollutants as individual compounds, total petrol hydrocarbons (TPH) are mixtures of a large number of hydrocarbons (saturated, unsaturated, and cyclic) with variable environmental fates and toxicity. TPH concentrations occurring in street runoff can be significantly higher, up to 25.9 mg L\(^{-1}\) (Sablayrolles et al. 2014). Because of their first flush behaviour, TPH reach the water as a shock load by stormwater discharge from traffic areas (Kayhanian et al. 2015). With regard to the expected toxic effects, TPH make higher demands on decentralized stormwater treatment systems (Dorchin & Shanas 2010).

In this study, the performance of hydrocarbon adsorption was investigated in column tests using six different adsorbents: activated carbon, activated lignite, exfoliated graphite, zero valent iron, and two different mixtures of haematite/amorphous ferric hydroxide (Fe\(_2\)O\(_3\)) and activated alumina (Al\(_2\)O\(_3\)). The objectives were (a) to evaluate the rate and capacities of hydrocarbon uptake, (b) to analyse the physical characteristics of the adsorbents, and (c) to verify the adsorption behaviours using a suitable adsorption model.

As a model compound, light fuel oil, a mixture of aliphatic, alicyclic, or aromatic hydrocarbons, was used to represent the hydrocarbons, especially the TPH. Because it contains fractions of chain length C\(_{10}\)–C\(_{40}\), light fuel oil is also used for testing oil and petrol separators. Owing to their chemical and hydrophobic properties, TPH can also represent other organic micropollutants, e.g., polycyclic aromatic hydrocarbons, because naphthalene and pyrene are constituents of light fuel oil.

### MATERIALS AND METHODS

#### The adsorbents

Six different adsorbents or mixtures of adsorption materials have been investigated for the retention of organic micropollutants. Granular activated lignite (HOK®, RWE Power AG, Germany) originates from lignite processing. Granular activated carbon (FILTRASORB® 300, Chemviron Carbon GmbH, Germany) is produced from bituminous coal. Exfoliated graphite (Graphit Kropfmühl AG, Germany) is prepared by rapidly heating sulphuric acid–graphite intercalation compounds. Zero valent iron (Gongyi Fengtai Refractories Abrasive & Trade Co., Ltd, China) is produced by directly reducing iron ore (magnetite). Furthermore, two mixtures of sorption materials (ADS 1 and ADS 2), which are currently used in stormwater treatment systems for heavy metal removal, were investigated. With a weight fraction of approximately 60%, the main reactive compounds of ADS 1 and ADS 2 are haematite/amorphous ferric hydroxide (Dr Ecker GmbH, Germany) and activated alumina (Martinswerk GmbH, Germany), respectively (Table 1). The remaining components of ADS 1 and ADS 2 are aerated concrete (30%) and granular activated carbon (10%), respectively.

#### Adsorbent characterization

To analyse the surface morphology of the adsorption materials, images of complex surface structures were examined by scanning electron microscope (SEM, Zeiss, LEO 1530 Gemini FESEM, Germany). The specific surface areas and pore volumes of the adsorbents were determined on the basis of nitrogen adsorption at 77 K using a surface

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### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Activated lignite</th>
<th>Activated carbon</th>
<th>Exfoliated graphite</th>
<th>Zero valent iron</th>
<th>ADS 1 (Fe(_2)O(_3))</th>
<th>ADS 2 (Al(_2)O(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
<td>88.40</td>
<td>87.88</td>
<td>94.58</td>
<td>0.30</td>
<td>7.09</td>
<td>4.98</td>
</tr>
<tr>
<td>H %</td>
<td>0.30</td>
<td>0.30</td>
<td>0.14</td>
<td>&lt; 0.1</td>
<td>1.41</td>
<td>1.35</td>
</tr>
<tr>
<td>N %</td>
<td>0.30</td>
<td>0.60</td>
<td>0.99</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>S %</td>
<td>0.30</td>
<td>0.70</td>
<td>5.17</td>
<td>–</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Particle size mm</td>
<td>1–2.5</td>
<td>1–2.5</td>
<td>0.5–2.5</td>
<td>0.75–2</td>
<td>1–5</td>
<td>1–5</td>
</tr>
<tr>
<td>BET specific surface area m(^2) g(^{-1})</td>
<td>279</td>
<td>1116</td>
<td>8.7</td>
<td>&lt; 1</td>
<td>36</td>
<td>124</td>
</tr>
<tr>
<td>Pore volume cm(^3) g(^{-1})</td>
<td>0.18</td>
<td>0.62</td>
<td>0.03</td>
<td>0.01</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>Average pore diameter, based on pore volume nm</td>
<td>2.5</td>
<td>2.2</td>
<td>14.55</td>
<td>6.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Porosity %</td>
<td>51.22</td>
<td>60.84</td>
<td>–</td>
<td>12.36</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
area analyser (ASAP 2010, Micromeritics, USA). The specific surface areas were calculated by following the Brunauer–Emmett–Teller (BET) method (Brunauer et al. 1938). The pore volumes were calculated using the Barrett–Joyner–Halenda theory (Barrett et al. 1951). The carbon, hydrogen, and nitrogen contents were determined with a CHN elemental analyser (vario EL, Elementar Analysensysteme GmbH, Germany).

The adsorbate

Light fuel oil, as a model compound for hydrocarbon pollutants in stormwater, was purchased from BP Europe SE (Germany). In addition, deionized water (ELGA LabWater, Purelab Option E50, 15 MΩ cm) was used.

The hydrocarbon oil index (HOI) of the hydrocarbons was determined according to German standard DIN EN ISO 9377-2 (2000). The HOI is defined as the total amount of compounds that can be extracted from a sample by a non-polar solvent with a boiling point between 39 and 69 °C and that are not adsorbed on Florisil. The index is the number of compounds with retention times between those of n-decane (C_{10}H_{22}) and n-tetracontane (C_{40}H_{82}).

Water samples were extracted after the pH was adjusted to 2 and 80 g of magnesium sulphate hepta-hydrate (MgSO_{4·7}H_{2}O) was added. The extract was transferred into a vial and cleaned up in a column filled with 2 g of Florisil. The purified aliquot was analysed by capillary chromatography using a gas chromatograph (Thermo Trace GC Ultra with amionization detector, analytical column: column UFM M-1/0.25/5x 0.32 Det). The detection limit was 0.1 mg L^{-1}.

The adsorption experiments

The sorption isotherm and kinetics of the TPH were determined in column experiments. Figure 1 shows the experimental setup.

To disperse the light fuel oil in water, the hydrocarbon solution (500 mL) was stirred and pumped upstream through the adsorption column (inner diameter, 1.5 cm; height, 10 cm). The adsorbent (5 g) was held between two fritted glass filters (P0, 160–250 μm). The pump’s flow rate was set to 5.3 mL s^{-1} (PLP 66, Behr Labortechnik GmbH, Germany). The sorption capacity of exfoliated graphite is strongly dependent on its bulk density (Toyoda et al. 2000). Therefore, the adsorbents were filled loosely, i.e., without compacting in the adsorption column, to avoid density effects. The initial pH was adjusted to 7.00 ± 0.05 using a dihydrogen phosphate/hydrogen phosphate buffer solution (KH_{2}PO_{4}/Na_{2}HPO_{4}) (Merck, Germany). The experiments were performed in duplicate at 22 ± 1 °C.

The maximum adsorption capacity

To determine the adsorption equilibrium isotherm of TPH onto the investigated sorption materials, the initial soluble concentration (C_0, mg L^{-1}) of TPH was varied. It ranged from 100 to 42 g L^{-1}. The adsorbent concentration (C_A) was 10 g L^{-1}. The column was streamed upstream for 24 hours to ensure equilibrium conditions. Then, the soluble concentrations (C_e, mg L^{-1}) were determined. From the equilibrium data, the specific adsorption capacity (q_e, mg g^{-1}) was calculated as follows:

\[ q_e = (C_0 - C_e)/C_A \]

The adsorption kinetics

Adsorption kinetic experiments were performed using different initial soluble organic micropollutant concentrations. In these experiments, the tested initial concentration (C_0) of TPH was 100 mg L^{-1}; at times \( t = 2, 3, 5, 10, 15, 30, 60, \) and 120 min, samples were taken to measure the soluble organic micropollutant concentration (C_t, mg L^{-1}). The specific removal rate (R_t, %) was calculated as follows:

\[ R_t = (C_0 - C_t)/C_0 \cdot 100(%) \]

The adsorption isotherms

The Langmuir and Freundlich isotherm models were used to describe the maximum adsorption capacity of the different sorption materials. The linear Langmuir isotherm (Langmuir 1932) describes the physisorption of neutral particles,
that is, molecules or atoms, by the sorbent surface, which is characterized by energetically homogeneous sorption sites. In addition, only a monomolecular coverage of the adsorbent surface is assumed. The Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants; it is found by applying the following equations.

\[ q_e = \frac{q_m \cdot (K_L \cdot C_e)}{1 + K_L \cdot C_e} \]  \hspace{1cm} (3)

\[ \frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \left( \frac{C_e}{q_m} \right) \]  \hspace{1cm} (4)

where \( q_e \) (mg g\(^{-1}\)) is the amount of organic micropollutant adsorbed, \( q_m \) (mg g\(^{-1}\)) is the maximum specific adsorption capacity, \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of the organic micropollutant and \( K_L \) (L mg\(^{-1}\)) is the Langmuir sorption coefficient. Linear graphs of \( C_e/q_e \) vs. \( C_e \) were used to calculate the parameters of the Langmuir isotherm by linear regression.

The Freundlich isotherm (Freundlich 1907) takes into account the fact that less sorbate may be adsorbed at a higher sorption surface load. Owing to its logarithmic growth, a complete loading of the sorption surfaces cannot be depicted. The Freundlich isotherm is expressed by Equations (5) and (6).

\[ q_e = K_F \cdot C_e^{1/n} \]  \hspace{1cm} (5)

\[ \log q_e = \log K_F + \frac{1}{n} \cdot \log C_e \]  \hspace{1cm} (6)

where \( q_e \) (mg g\(^{-1}\)) is the amount of organic micropollutant adsorbed and \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of the organic micropollutant. The Freundlich sorption coefficient \( K_F \) (mg g\(^{-1}\)·L mg\(^{-1}\)^{1/n}) is correlated with the quantity of sorbate associated with the adsorbent. The Freundlich exponent 1/n (dimensionless) is related to the sorption strength at a particular temperature.

RESULTS AND DISCUSSION

Physical characterization of the adsorbents

Scanning electron micrographs of the investigated adsorbents and their surfaces show that activated carbon (Figure 2(a)) and activated lignite (Figure 2(b)) particles are angular and exhibit rough surfaces. In contrast, the particles of exfoliated graphite have worm-like appearances (Figure 2(c)). Exfoliated graphite exhibits a characteristic smooth texture with larger pores evident (Toyoda et al. 2000).

Figure 2(d) shows the sponge-like surface of zero valent iron, which contains few macropores. In contrast, Fe₂O₃ (Figure 2(e)) and Al₂O₃ (Figure 2(f)) have highly irregular surfaces. The differences between the adsorbent surfaces...
are also reflected in their physical characteristics, such as pore volume, distribution, and porosity, which are essential to elucidating the behaviours of adsorbents in the adsorption process. Table 1 summarizes the BET surface areas and pore volumes of these six adsorbents. Activated carbon has the highest BET surface area at 1,116 m$^2$ g$^{-1}$, followed by HOK at 279 m$^2$ g$^{-1}$, ADS 2 at 124 m$^2$ g$^{-1}$, and ADS 1 at 36 m$^2$ g$^{-1}$. Exfoliated graphite and zero valent iron have low BET surface areas with 8.7 m$^2$ g$^{-1}$, and $<1$ m$^2$ g$^{-1}$, respectively. In addition, activated carbon has the highest pore volume at 0.62 cm$^3$ g$^{-1}$. The pore volume of activated lignite is significantly lower at 0.18 cm$^3$ g$^{-1}$, followed by ADS 1 at 0.18 cm$^3$ g$^{-1}$, and ADS 2 at 0.16 cm$^3$ g$^{-1}$. Exfoliated graphite and zero valent iron have very low pore volumes of 0.03 and 0.01 m$^3$ g$^{-1}$, respectively. A large BET surface area and high pore volume suggest a high adsorption capacity.

**Maximum adsorption capacities**

Figure 3 depicts the adsorption of light fuel oil onto the various adsorbents at the highest initial concentrations. It is evident that the adsorption capacities were not reached. The materials were not saturated despite the very high initial concentrations of TPH. In the current assessment, exfoliated graphite has the highest adsorption capacity for TPH at 3,850 mg g$^{-1}$ ($C_0 = 42,000$ mg L$^{-1}$) with a high specific removal rate ($R_r$) of 91.7%. Owing to its comparatively low initial concentration and the strong dependence of its sorption rate on its bulk density, the maximum adsorption capacity of exfoliated graphite is much lower than it was found to be in other studies (Toyoda et al. 2000). This adsorbent was packed loosely in the glass column without adjustment of its bulk density. A higher bulk density would lead to better performance but also to a decreased permeability. The retention and hydraulic aspects must be considered together for materials used in treatment systems.

In contrast to exfoliated graphite, activated carbon exhibited a lower adsorption capacity of only 1,750 mg g$^{-1}$ ($C_0 = 31,500$ mg L$^{-1}$, $R_r$ of 55.6%). Ayotamuno et al. (2006) observed a maximum capacity of 1,632 mg g$^{-1}$ ($C_0 = 9,305$ mg L$^{-1}$, $R_r$ of 87.7%) for the adsorption of crude oil to granular activated carbon. Activated lignite and ADS 2 showed a moderate retention of 42.9% ($C_0 = 31,500$ mg L$^{-1}$). ADS 1 and zero valent iron showed the lowest adsorption capacities of 1,250 and 800 mg g$^{-1}$, respectively.

The adsorption capacity of exfoliated graphite was found to be very high compared to the other adsorbents investigated. In many cases, carbon-based adsorbents were used for the removal of micropollutants from runoff due to their large surface area, pore volume, and broad range of surface functional groups (Pehlivan & Arslan 2007; De Ridder et al. 2012). In contrast to organic trace pollutants such as PAH, which favour binding on micropores (Ania et al. 2007), petrol hydrocarbons use macropores as active sites in their adsorption processes (Toyoda et al. 2000). Nishi et al. (2002) found that the optimal pore radius for the kinetics of heavy oil sorption is between 50 and 100 μm. Macropores are required for the adsorption of TPH. A pre-selection of the adsorbent based on its BET surface area and pore volume is not useful because these macropores remain unaccounted for in the BET method.

To verify the experimental data, the Freundlich and Langmuir isotherms were calculated for the six tested materials (Table 2). The results show that the Freundlich and Langmuir models are both suitable for describing the adsorption of TPH onto the adsorbents. The calculated Langmuir isotherm tends to agree better with the experimental data, indicating monolayer coverage of TPH on the adsorbent’s surface. Overall, the maximum adsorption capacity calculated by the Langmuir model for, for example, activated carbon (1750 mg g$^{-1}$) was in the range of the experimentally determined values (1,667 mg g$^{-1}$). Only the adsorption characteristics of exfoliated graphite are not reflected correctly because the maximum capacity was not reached.

**The adsorption kinetics**

To investigate the adsorption kinetics, experiments were performed with an initial TPH concentration ($C_0$) of 100 mg L$^{-1}$. For all of the adsorbents, similar adsorption kinetics were observed that consisted of two phases (Figure 4). An initial fast rate of TPH removal was followed by a slower uptake reaction before equilibrium was reached.
established. Similarly, other investigators reported that the elimination of heavy metals and PAH is a two-step reaction involving a fast initial disappearance followed by a slow removal process (Luna et al. 2008).

Exfoliated graphite has the fastest removal rate. Within 5 min, 98.4% of the hydrocarbons were retained. This corresponds to an adsorption rate of 1.97 mg g⁻¹ min⁻¹. Activated carbon has an adsorption rate of 1.63 mg g⁻¹ min⁻¹. Activated lignite and ADS 2, adsorbents with similarly high adsorption capacities, have significantly slower retention rates, with adsorption rates based on a 5 min contact time of 0.43 mg g⁻¹ min⁻¹ and 0.08 mg g⁻¹ min⁻¹, respectively. ADS 1 and zero valent iron have a removal rate of 0.40 mg g⁻¹ min⁻¹ and 0.75 mg g⁻¹ min⁻¹, respectively.

For application of the adsorbents in compact filter systems, it should be considered that the TPH concentrations in real road runoff (with a median value of 0.5 up to 25.9 mg L⁻¹) are well below the concentration examined (Sablayrolles et al. 2011). This results in a much lower removal rate, which requires a larger contact time between the filter and the organic pollutant. High sorption rate and adsorption capacity are crucial for the selection of the adsorbents for an effective treatment of road runoff. This can be investigated by column experiments. The adsorbents can be pre-selected by their physical characteristics, in particular by the number of macropores.

### CONCLUSION

The efficiency of various adsorbents at remove TPH from water was studied for use in a stormwater treatment system. Column experiments were conducted to investigate the adsorption capacity and velocity of the potential filter materials.

The following conclusions demonstrate the significant findings of this study:

1. The exfoliated graphite used in the experiments shows the best adsorption performance at removing hydrocarbons from solution. With almost complete retention and the fastest removal rate, exfoliated graphite was much more efficient than activated carbon. This effect is due to its high number of macropores, which are crucial for the adsorption of hydrocarbons.

2. Macropores are essential for the adsorption of TPH, unlike for dissolved substances such as heavy metals. A pre-selection of the adsorbent based on its BET surface area and pore volume is not useful because these macropores remain unaccounted for in the BET method.

3. The Freundlich model and the Langmuir model are both suitable for describing the adsorption of petroleum hydrocarbons. The calculated Langmuir isotherm tends to agree better with the experimental data, thus indicating the applicability of monolayer coverage of TPH on the adsorbent’s surface.
Owing to its high adsorption capacity and sorption rate, exfoliated graphite is suitable for practical use in decentralized stormwater treatment systems. Because the residence time in a decentralized treatment system and, therefore, the contact time between sorbent and organic micropollutant are relatively short, the adsorption rate is becoming more important. Nevertheless, the maximum adsorption capacity is also essential for a long-term efficient treatment system.

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