Performance of novel media in stratified filters to remove organic carbon from lake water

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ABSTRACT

Disinfection by-products (DBPs) are an ever-increasing occurrence in water networks, particularly those which abstract water from peatland areas. Although much research has been carried out to discover novel methods to remove specific DBPs, the removal of natural organic matter (NOM) from source water may provide a more sustainable solution in many areas. This study focuses on the removal of NOM by novel filters, which could be retroactively fitted to any conventional water treatment facility. The filters comprised stratified layers of a variety of media, including sand, Bayer residue, granular activated carbon (GAC), and pyritic fill. The filters were operated under two loading regimes, continuous and intermittent, at loading rates similar to recognised design standards. The most successful filter design comprised stratified layers of sand, GAC, and pyritic fill. Over the duration of a 240 day study, these filters obtained average dissolved organic carbon removal rates of 40%, and achieved average specific ultra-violet absorbance reductions from 2.9 to 2.4 L mg⁻¹ m⁻¹. The study demonstrates that these novel filters may be used to reduce NOM levels, thus reducing the potential for DBP formation. Such designs can incorporate the use of waste media, making the overall design more sustainable and robust.

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1. Introduction

The majority of water treatment plants (WTPs) use ground water or surface water, which can contain fluctuating amounts of total organic carbon (TOC), as their source. Organic carbon enters water bodies by leaching from land, particularly from peatlands, and concentrations in source water can fluctuate depending on temperature, rainfall and depth to water table (Grand-Clement et al., 2014). Organic carbon in a WTP can increase disinfection demand, act as a precursor to disinfection by-products (DBPs), and be responsible for membrane fouling and corrosion (Matilainen et al., 2010; Velten et al., 2011). The presence of DBPs in drinking water may have numerous ill-effects on human health. These include bladder cancer, genetic mutations, and foetal abnormalities (Grellier et al., 2015; Richardson et al., 2007).

Disinfection by-products are a concern internationally, with many countries supporting the implementation of more stringent legislation regarding DBPs in potable water (Ecorys, 2015), and are responsible for the majority of non-compliance with regulatory standards in many WTPs (EPA, 2015). Disinfection by-products occur when microparticles in water react with disinfection chemicals, such as chlorine (Kim et al., 2002). There are over 600 identified DBPs, but most are not currently regulated (Deborde and von Gunten, 2008; Hrudey, 2009). The most common-forming DBPs occur when natural organic matter (NOM) reacts with chlorine, forming compounds such as trihalomethanes (THM) and haloacetic acids (HAA) (Deborde and von Gunten, 2008). Currently, HAA, bromate, chlorite, and THM are regulated in the USA, where the maximum allowable concentrations (MACs) are 0.06, 0.01, 1.0 and 0.08 mg L⁻¹, respectively (USEPA, 2009). However, to date, THM and bromate are the only DBPs regulated by the European Union (EU), where the limit for THM is 0.1 mg L⁻¹ and the limit for bromate is 0.01 mg L⁻¹ (SI No 278 of 2007, 2007).

The composition of NOM is important when assessing the potential for formation of DBPs (Tran et al., 2015). Natural organic matter is commonly measured as organic carbon, either total (TOC) or dissolved organic carbon (DOC). Dissolved organic carbon is the most concerning element, as the larger particles are much easier to remove in a standard treatment process such as coagulation or straining by filtration (Matilainen et al., 2010), thus smaller particles and dissolved matter are more likely to form DBPs (Gopal et al., 2010).
As research into the process of DBP formation and removal intensifies, there has been much investigation into NOM fractionation and characterisation, to specify which molecules are more likely to react with chlorine, and to form DBPs (Tran et al., 2015). A disadvantage to this approach is that the methods used to fractionate NOM are generally costly and/or require specific expertise. A more accessible indicator is the relationship between ultraviolet absorbance at a wavelength of 254 nm (UVA254) and DOC, known as accessible indicator. The disadvantage to this approach is that the methods used to fractionate NOM are generally costly and/or require specific expertise. A more accessible indicator is the relationship between ultraviolet absorbance at a wavelength of 254 nm (UVA254) and DOC, known as accessible indicator (Hua et al., 2015). SUVA can be used to investigate the potential for formation of DBPs by acting as an indicator of the aromaticity and hydrophobicity of the water (Anumol et al., 2015; Christy et al., 1999), as it is most commonly found that the hydrophobic organic compounds have higher THM reactivity than hydrophilic organic compounds (Tran et al., 2015). It also has the practical advantage of using commonly available laboratory instruments (Hua et al., 2015). Hydrophobic acids, as well as hydrophilic acids with high SUVA, have high DBP formation potential (Zhang et al., 2009). Both the United States and the Irish Environmental Protection Agency (EPA) use SUVA analysis to determine the level of treatment required to avoid DBP formation (EPA, 2011; USEPA, 2006).

Many treatment technologies, such as dissolved air flotation, membrane filtration, ultrafiltration, and oxidation (Matilainen et al., 2010), have been designed to focus on the removal of organic carbon or DBPs. Although these technologies can prove successful under some operational conditions (for example, ultrafiltration is prone to fouling under high suspended solids and turbidity conditions (Tian et al., 2013), many have high capital and maintenance costs. A relatively low cost alternative in WTPs is the use of traditional sand filters, but they are not as successful in DOC removal (e.g., 10–50%) (Kim and Kang, 2008; Teksoy et al., 2008). The use of alternative media may allow the use of such low-cost technologies, while achieving DOC removal. Based on adsorption testing carried out by Grace et al. (2015), it was decided to investigate the use of Bayer residue (a waste product from the aluminium processing industry) and pyritic fill (a waste product of the construction industry), with granular activated carbon in a filter system, in the current study.

The aim of this study was to design, operate and monitor the performance of filters, operated in intermittent and continuously loaded regimes at pilot-scale, containing media chosen to optimise DOC removal and to prevent surface clogging. Two configurations were chosen, one containing equal layers of sand, Bayer residue and pyritic fill, and the other containing sand, GAC and pyritic fill. The filter configurations were based on bench- and laboratory-scale studies (Grace et al., 2015), and were operated at a WTP.

### Table 1

<table>
<thead>
<tr>
<th>Media characteristics (Grace et al., 2015)</th>
<th>Coarse sand&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Pyritic fill&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Bayer residue&lt;sup&gt;e&lt;/sup&gt;</th>
<th>GAC&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>97.72</td>
<td>74 ± 10</td>
<td>8.9</td>
<td>–</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.26</td>
<td>2.9 ± 1.5</td>
<td>43.8</td>
<td>–</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.21</td>
<td>7.6 ± 0.9</td>
<td>15.04</td>
<td>–</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.05</td>
<td>1.05 ± 0.15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LO&lt;sub&gt;L&lt;/sub&gt;&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.36</td>
<td>–</td>
<td>9.5</td>
<td>–</td>
</tr>
<tr>
<td>CaO</td>
<td>–</td>
<td>5.4 ± 5.1</td>
<td>6.6</td>
<td>–</td>
</tr>
<tr>
<td>MgO</td>
<td>–</td>
<td>0.6 ± 0.14</td>
<td>0.99</td>
<td>–</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>–</td>
<td>0.3 ± 0.15</td>
<td>3.3</td>
<td>–</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>–</td>
<td>0.3 ± 0.03</td>
<td>9.2</td>
<td>–</td>
</tr>
<tr>
<td>MnO</td>
<td>–</td>
<td>0.05 ± 0.05</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>–</td>
<td>7.6 ± 5.7</td>
<td>0.41</td>
<td>–</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>–</td>
<td>–</td>
<td>0.36</td>
<td>–</td>
</tr>
<tr>
<td>Iodine No (mg gm&lt;sup&gt;–1&lt;/sup&gt;)</td>
<td>–</td>
<td>–</td>
<td>1100</td>
<td>–</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>–</td>
<td>–</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>–</td>
<td>–</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>Effective size (mm)</td>
<td>1.31</td>
<td>0.34</td>
<td>0.06</td>
<td>0.58</td>
</tr>
</tbody>
</table>

<sup>a</sup> Irwin’s Quality Aggregates.

<sup>b</sup> Sandberg LLP.

<sup>c</sup> Rusal Aughinish.

<sup>d</sup> Indo German Carbons Ltd.

<sup>e</sup> Loss on Ignition.

### 2. Materials and methods

#### 2.1. The study site and context

The WTP examined in this study has a source which contains NOM and has existing practices in place for mitigating THM formation. It currently uses ozonation, followed by GAC filtration to reduce the chlorine consumption of treated water, by removing biodegradable organics (Bourbigot et al., 1986), thereby reducing the likelihood of DBP formation. However, GAC exhausts quickly and requires excessive capital, which can make be costly and unsustainable to operate (Corwin and Summers, 2010).

#### 2.2. Filter construction

Two novel filter configurations, each constructed in triplicate (i.e. n = 3 for each configuration), were operated under intermittent...
and constant loading regimes (Fig. 1). Intermittently loaded filters were investigated, as they are commonly used in wastewater treatment, and may be more applicable for instances requiring less water or for household point-of-use systems (Sobsey et al., 2008). Both configurations were 1 m deep and each comprised three 0.33 m deep layers. ‘Design A’ contained (from the surface downwards) layers of sand, Bayer residue, and pyritic fill. ‘Design B’ contained (from the surface downwards) layers of sand, GAC, and pyritic fill in equal layers. These media were chosen based on bench- and laboratory-scale testing. Both sets of filters were instrumented with sample ports at the media interfaces. The aim of the sample port analysis was to investigate where the majority of the removal was occurring, with a view to further improve the design. After 100 days of operation, 1 m deep sand filters (the study control) were constructed, which were operated under both loading regimes (n = 3 in each regime). This enabled comparison between the performances of the novel filters against conventional sand filters. The sand (for the control filters) had an effective particle size (d10) of 0.18 mm and a uniformity coefficient of 2.19, as per Irish EPA guidelines (EPA, 1995). The constantly loaded filters had a freeboard depth of 0.7 m above the surface of the media. Media characteristics are presented in Table 1. The study ran for a total of 240 days from June to February, and during that time the temperature ranged from 1.3 °C to 20.9 °C (Met Eireann, 2016).

2.3. Filter operation

Each set of filters was loaded with untreated lake water (the average water composition over the duration of the study is detailed in Table 2). A holding tank was filled daily using a surface-mounted continuous duty pump (Antares, model no 140608777) and water was then pumped onto each filter according to its loading regime. The constantly loaded filters were kept under a constant head of 0.5 m of supernatant water. This was controlled by the installation of overflow lines. The constantly loaded filters were loaded with a multichannel peristaltic pump (7528-10, Masterflex L/S Variable-Speed Drive). The intermittent filters were timer-controlled, and were dosed for 2 min every 2 h using a submersible pump (4011708104033, Eheim Compact 1000 L h−1). Each set of filters had a hydraulic loading rate (HLR) of 0.1 m h−1, as recommended by the Irish EPA for slow sand filtration for water treatment (EPA, 1995).

2.4. Water contaminant analysis

Water samples were taken on a weekly or bi-weekly basis from the base of each filter and the raw water source and every three weeks from sample ports. The pH of each sample was recorded (Eutech pH 700 m), and the samples were filtered through 0.45 μm filter paper (11406–47–ACR). Phosphate-phosphorus (PO4−P), nitrate-nitrogen (NO3−N), nitrite-nitrogen (NO2−N), ammonium-nitrogen (NH4−N), and alkalinity were analysed using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Dissolved organic carbon, dissolved inorganic carbon (DIC), total phosphorus (TP) and total nitrogen (TN) were analysed using a TOC analyser (BioTector Analytical Systems Ltd). UVA254 absorbance was measured using a UV–Visible spectrophotometer (Cary 50, Agilent Technologies), using a quartz sample cell with a path length of 10 mm. Metal analysis was carried out on water samples over the first 63 days of operation, using ICP-MS, in order to ensure there was no heavy metal leaching from the media into the effluent water. Samples could only be taken from sample ports in the continuously loaded filters, as sufficient volume could not be extracted from the intermittently loaded columns for DOC
3. Results and discussion

3.1. Influent characteristics

Influent characteristics of the source water are presented in Fig. 2 (with reference to ambient temperature and rainfall). The DOC concentrations in the lake water varied significantly over the course of the study, with the highest concentration occurring at day 239 after a series of rainfall events in January/February (Fig. 2). Trends of DOC are known to change seasonally, and previous studies have reported decreases in Autumn and Spring (Eimers et al., 2008), and increases in November and May (Brooks et al., 2015). Evidently, the concentration of DOC is dependent on many variables, making it more difficult to design a treatment system that can work efficiently across a large concentration range. The average range in the influent water in the current study was 9.9 mg L\(^{-1}\) (over a range of 6.8 mg L\(^{-1}\)), over a period of 240 days.

3.2. Filter performance

Table 2 describes the overall performance of each filter design, under both loading regimes from day 100 to day 240. The concentrations of nutrients in the influent lake water were negligible, making it difficult to draw specific conclusions regarding the performance of the filters. Dissolved organic carbon decreased and DIC increased from influent to effluent, in each of the filter configurations. The absorbance of UV light at 254 nm and the SUVA decreased in both of the filter configurations, but increased in the control filters. Alkalinity and pH increased slightly as the water travelled through the filters, in all cases, which may be attributed to leaching from media.

3.2.1. Dissolved organic carbon removal

Both filter configurations successful in the removal of DOC (Table 2 and Fig. 3), and their performance exceeded that of the study controls. When the filters were loaded continuously, Designs A and B achieved average removals of 27 and 40%, respectively. When operated with an intermittently loaded regime, average removal rates of 31% were achieved in Design B. In comparison, DOC removals from the control filters ranged between 4% and 9% in each loading regime.

Mass removals of DOC are presented in Fig. 4. Design B had significantly better DOC mass removals than Design A (\(p = 0.009\)) and the control filters in both operational regimes (\(p = 0.001\) and \(p = 0.0\), for intermittent and continuous loading, respectively). The loading regime did not have a significant impact on the mass removal rates in Design B, which averaged at 8.8 and 7.6 g m\(^{-2}\) day\(^{-1}\) for the continuous and intermittently loaded filters, respectively (\(p = 0.168\)). There was no significant difference between the mass removal rates of the control filters under either continuous or intermittent loading regimes (\(p = 0.349\)).

Dissolved organic carbon removal was expected in each of the novel configurations, based on adsorption data from an earlier study (Grace et al., 2015), and in particular in Design B, based on previous studies using GAC for carbon removal (Gibert et al., 2013; Velten et al., 2007). The removals were similar to those achieved by
Kim and Kang (2008), who measured DOC removal of 49% for the first 3 months of operation, 30% for the following 3 months, and 21% thereafter. Similar removal rates were achieved by Tansakul et al. (2011), who used powdered activated carbon (PAC) as a pre-treatment to ultrafiltration, although when the dosage of PAC was doubled and quadrupled, removal efficiencies increased to 70%. However, ultrafiltration can be prone to fouling quickly. An increase in DIC in the effluent was observed throughout the experiment. For GAC filtration, it is understood that the removal mechanism for DOC begins with the physio-chemical adsorptive mechanisms, but after a certain period, the stronger mechanism is microbial activity, which feed on NOM (Boon et al., 2011; Velten et al., 2007). This may attribute to the increase in DIC. Dissolved inorganic carbon can be characteristic of microbial degradation, where carbon dioxide mineralisation has occurred, and also where DOC has photo-oxidised to DIC (Granéli et al., 1996; Hansell et al., 2004).

3.2.2. SUVA analysis

The SUVA analysis is presented in Fig. 5. In almost all instances, the effluent SUVA was less than the influent. The highest reduction occurred in Design B, both in the continuous and the intermittently loaded filters, where the average concentrations reduced from 2.9 to 2.4 L mg⁻¹ m⁻¹ (Table 2) (p = 0.01 and p = 0.03). The loading regime did not have a significant impact on SUVA reduction (p = 0.9). Design A, operated in the continuous loading regime, also achieved an average SUVA reduction to 2.6 L mg⁻¹ m⁻¹ (p = 0.096). These results are comparable to results reported by Liu et al. (2016), who measured a SUVA reduction from 3 to 2.4 L mg⁻¹ m⁻¹, using zero valent iron with interspersed carbon cathodes. The same study reported better DOC removal, with efficiencies of 61%, starting from a DOC concentration, similar to this study, of 11.2 mg L⁻¹. Results from a WTP in Greece reported a SUVA reduction of 2.22 to 1.26 L mg⁻¹ m⁻¹ (Papageorgiou et al., 2016), from the beginning of the treatment plant until the end, using pre-
ozonation, sand filters, ozonation and GAC filters. This indicates that in a full-scale treatment works, the novel designs presented in this study could be very effective. Papageorgiou et al. (2016) also noted an increase in SUVA following sand filtration, again reflective in the results of the current study.

3.2.3. Sample port analysis

The results of the sample port analysis, for the full duration of the study, are presented in Fig. 6. For both Designs A and B, the top sand layer had poor removal of DOC, and sometimes even desorbed or leached DOC. This was to be expected, based on adsorption testing results reported in Grace et al. (2015), and issues faced by WTPs in general. However, the sand was necessary in order to mitigate any potential clogging issue, and to strain the larger particles, if present, from the influent.

In Design A, the removal of DOC by Bayer residue varied considerably throughout the duration of the experiment, and appeared to desorb DOC at times. This could potentially be mitigated by a redesign, or by combining the medium with another to harness the adsorption potential that is present. For other contaminants, a pre-treatment, or activation, of Bayer residue has proved successful (Huang et al., 2008; Li et al., 2006), which could also be put in place. In Design B, GAC had good removal of DOC from the influent. This was in line with results from Grace et al. (2015) and other studies (Kennedy and Summers, 2015; Kim and Kang, 2008; Lin et al., 2010). In both Design A and B, pyritic fill also had good DOC removal. Pyritic fill is not commonly used in treatment of water or wastewater, and to date, there has been little investigation into its use as an adsorbent. From the port analysis study, it is clear that GAC has the greatest potential for DOC removal, followed by sand and pyritic fill.

3.3. Metal analysis

Metal analysis is presented in Table S1. Design A leached aluminium (Al) and iron (Fe) into the water over the first 63 days of
The Fe returned to an acceptable level after 21 days, and although the Al reduced, it was still above the threshold for safe drinking water (0.2 mg L\(^{-1}\)) ([SI No 278 of 2007, 2007]). The presence of metals in Design A was due to the presence of Bayer residue. This is a by-product of the Al production industry, and also contains high levels of Fe ([Table 2] (EAA, 2013)). Bayer residue may also be prone

![Fig. 5. SUVA values from influent and effluents.](image)

![Fig. 6. DOC analysis from sample ports in continuously loaded filters.](image)

**Table 4**

<table>
<thead>
<tr>
<th>Depth below surface (mm)</th>
<th>Continuous</th>
<th>Intermittent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Design A ((K_s/K_v))</td>
<td>Design B ((K_s/K_v))</td>
</tr>
<tr>
<td>0–50</td>
<td>1</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>50–100</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>100–150</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

operation. The Fe returned to an acceptable level after 21 days, and although the Al reduced, it was still above the threshold for safe drinking water (0.2 mg L\(^{-1}\)) ([SI No 278 of 2007, 2007]). The presence of metals in Design A was due to the presence of Bayer residue. This is a by-product of the Al production industry, and also contains high levels of Fe ([Table 2] (EAA, 2013)). Bayer residue may also be prone
to allowing the accumulation of Mn, followed by the release of a high-concentrate precipitate (Komnitsas et al., 2004), further ruling it out for use. Although the presence of metals was concerning, an ion exchanger or polish filter could be added to the treatment system to mitigate the potential for metal leaching. It would also be possible to wash the filter out before use to clear any leaching metals. Design B did not leach any metals of concern, other than metals found in the influent.

3.4. Filter deconstruction

Filter deconstruction was carried out after the filters had been decommissioned. In all cases, little to no clogging was observed (Table 4), indicating that the hydraulic function of the filters was preserved throughout the loading period.

During deconstruction, samples were analysed for organic matter content to determine where the majority of the DOC was removed (Fig. 7). In the case of Design A, most of the organic matter remained at the surface (sand) layer, which could be due to both organic matter removal by physical filtration and biofilm build-up. The continuously loaded filters had a larger build-up than the intermittently loaded, indicating that the loading regime influenced this. Design B had the largest accumulation of organic matter in the second layer, composed of GAC. This was to be as expected, given that Design B was more successful in DOC removal, and that microbial layer was likely to be present on the GAC samples (Boon et al., 2011). There was little accumulation of organic matter in the pyritic fill layers. In the control filters, there was limited organic matter accumulation, which was due to the lack of DOC removal. Any accumulation that was present, existed on the surface layer,
was most likely due to straining and/or a biofilm build-up. This layer was evident on all filters, which was most likely due to straining and/or a biofilm build-up.

**4. Conclusion**

Effective DOC removal at water treatment plants is essential in order to prevent the formation of DBPs. Sand filters are not effective at reducing DOC to a sufficient level, as demonstrated by the control filters. Design A (sand, Bayer residue and pyritic fill) was reasonably effective at removing DOC under a continuous loading regime. Metal analysis indicated that there could be potential leaching from Bayer residue, resulting in the design being ruled out for potable water treatment.

Design B, comprising sand, granular activated carbon, and pyritic fill, was most effective. After a study period of 240 days, an average of 40% DOC removal was achieved, with no significant difference between the continuous and intermittent loading regimes. There was no metal leaching from this design. In practice, a continuous loading regime is more desirable as it requires less monitoring and can be more efficient than running a pump on/off cycles. Design B also achieved good SUVA reduction, from 2.9 to 2.4 L min⁻¹ m⁻¹. These results are comparable to other alternative technologies being investigated.

Further investigations should involve increasing loading rates to assess if the filters can be used for higher throughput, to investigate the filters under a rapid gravity system, and to assess where best to place the filters in the treatment process. The filters could be used in place of the conventional sand filters, but could also be used to reduce DOC concentrations, where concentrations are particularly high, to a point where other technologies will be successful.

This study concludes that a combination of media, including waste products, can be used for DOC removal, which is more effective than current sand filter designs. The resulting design is sustainable and efficient, and effectively removes DOC from surface water, reducing the potential for formation of DBPs.

**Appendix A. Supplementary data**

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.08.025.

**References**


