Effect of zero-valent iron amendment on the performance of biosand filters
Duithy George and M. Mansoor Ahammed

ABSTRACT
The study compared the performance of a biosand filter (BSF) with two BSFs modified by introducing a layer of zero-valent iron (ZVI) during a long-duration test (4 months) mimicking the household use pattern in developing countries. Results of the study showed that for bacterial removal, ZVI-amended BSFs outperformed the BSF by at least 1 log10 unit throughout the filter operation. Effluent turbidity in the BSF and modified BSFs was not significantly influenced by influent values for the turbidity range tested in the study (17.0–45.4 NTU). Removal efficiency of nitrates was higher in the modified BSFs, with up to ~89% removal in the modified BSFs compared with ~29% in the BSF. Sharp decline in dissolved oxygen (DO) was observed during the passage of water through the filters. The DO decline was more in the modified filters compared with the conventional BSF. Effluent iron remained within the drinking-water quality standards. The study thus indicates the potential of ZVI to improve the performance of BSFs.

Key words | bacteria, biosand filter, household water treatment, nitrate, turbidity, zero-valent iron

INTRODUCTION
A biosand filter (BSF) is an intermittently operated slow sand filter at small scale, and is one of the most promising and accessible technologies emerging for household water treatment. It is reported that more than 800,000 BSFs were in operation as of 2015, serving an estimated 5 million people in 60 countries (CAWST 2016). The BSF has become popular as it is easy to use and simple to maintain.

Several parameters influencing the performance of a BSF include sand size, hydraulic head, pause time, filter ripening, daily charge volume and raw water quality including turbidity (Jenkins et al. 2011). Several studies reporting on the performance of BSFs suggest that the BSF has limitations especially in terms of its microbial removal efficiency during the ripening period, which typically takes 4–6 weeks. Cleaning of the filter also impairs the performance of the filter for up to 4 weeks after cleaning. These findings raise questions about the assurance of safe water provided to users of BSFs before ripening and after cleaning (Elliott et al. 2008; Nair et al. 2014; Young-Rojanschi & Madramootoo 2014), and indicates the need for modification of the BSF in order to improve its performance.

Different methods have been adopted for improving the performance of the BSF. Jenkins et al. (2011) focused on flow control options, sand grain, size distribution, as well as pause period. Their results showed that lower flow rates increased removal. Napotnik et al. (2017) found that smaller sand bed depths in the bucket-sized filters did not impact filter performance with respect to turbidity and Escherichia coli removal. Ahammed & Davra (2011) modified a BSF with a 10-cm-thick layer of iron oxide-coated sand and showed that performance of the modified BSF compared with the BSF in bacterial reduction was always better by at least 1 log unit. Young-Rojanschi & Madramootoo (2014) reported that although biosand filters were developed for
intermittent operation, the filters performed significantly better when operated continuously.

Zero-valent iron (ZVI) has been applied to remediate contaminated groundwater and has shown good capacity to remove a broad range of organic and inorganic contaminants including microorganisms (You et al. 2005; Noubactep et al. 2012). Attempts have been made to modify BSF with ZVI. It has been shown that the use of ZVI improves the virus removal capacity in BSFs (Chiew et al. 2009; Bradley et al. 2011). Chiew et al. (2009) tested the efficacy of a biosand filter amended with ZVI nails for removing arsenic and microorganisms from groundwater and reported that the filters reduced bacterial pathogens, but not always to drinking water target levels. Bradley et al. (2011) showed that the virus removal efficiency by iron-amended biosand filtration depends on source water quality and the characteristics of iron added.

Nitrate contamination of drinking water is a widespread problem. It has long been known that levels of nitrates exceeding the 50 mg/L limit are associated with certain health problems. It is known that ZVI can effectively remove nitrates (Westerhoff & James 2005).

In the present study ZVI in two different locally available forms was introduced in a BSF in order to improve its performance. The study compared the reduction of bacteria, turbidity and nitrates by the BSF and modified BSFs during a long-duration test (4 months) mimicking the household use pattern in developing countries.

**MATERIALS AND METHODS**

Three full-scale BSFs – one conventional BSF and two ZVI-modified BSFs – were constructed using plastic containers of approximately 75 cm height following the specifications of the Centre for Affordable Water and Sanitation Technology (CAWST 2010). Plastic containers bought from the local market were used in the study. Locally available river sand passing through 1.18 mm and retained on 0.150 mm sieves was used. The sand was washed several times using tap water until the wash water became clean. One of the modified BSFs contained 7.5 kg of mild steel nails (BSF (nail)) and the other contained 7.5 kg of iron filing scrap (BSF (scrap)) which were mixed uniformly throughout the top 15 cm of the filter media, excluding a 5 cm layer of fine sand. Mild steel nails (20 mm long, 2 mm diameter) were purchased from the local market while iron filing scrap was obtained from the workshop of S. V. National Institute of Technology, Surat, India. Water was present inside the filter before loading to avoid any occurrence of air space and short circuiting. A plastic diffuser plate was then placed on the lip of the filter to avoid disturbance of the top layer during water loading of the filters. Figure S1 (Supplementary Material, available with the online version of this paper) shows the schematics of the modified BSF used.

**Filter operation**

Two filter runs of total 4 months duration were conducted with three filters under identical conditions at room temperature which varied in the range of 25–30 °C during the experiment. The influent characteristics of the water used in the two filter runs are presented in Table 1.

In Run 1, tap water spiked with potassium nitrate with a targeted initial nitrate concentration of 25 mg/L and initial turbidity of 20 NTU in the form of natural clay was used. Sewage at the rate of 1 mL/L of water was added. A daily charge of 20 L water was chosen based on the typical requirement of a developing country household. Also, it represents about one pore volume of about 19.5 L. In Run 2, in order to study the effect of influent turbidity on the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run 1 (Mean ± SD)</th>
<th>Run 2 (Mean ± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>22 ± 3</td>
<td>41 ± 2</td>
</tr>
<tr>
<td>pH</td>
<td>8.02 ± 0.4</td>
<td>7.75 ± 0.3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>26.9 ± 1.8</td>
<td>28.4 ± 1.6</td>
</tr>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>6.3 ± 0.6</td>
<td>6.5 ± 0.4</td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>26.0 ± 1.6</td>
<td>–</td>
</tr>
<tr>
<td>Ammonia (mg/L)</td>
<td>&lt; 0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Total iron (mg/L)</td>
<td>0.08 ± 0.04</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>Total coliforms (MPN/100 mL)</td>
<td>$1.5 \times 10^9 \pm 3 \ldots 10^7$</td>
<td>$1.5 \times 10^4 \pm 2.8 \times 10^2$</td>
</tr>
<tr>
<td>Faecal coliforms (MPN/100 mL)</td>
<td>1,515 ± 441</td>
<td>1,700 ± 566</td>
</tr>
<tr>
<td>Heterotrophic plate count (CFU/mL)</td>
<td>$2.3 \times 10^6 \pm 2.2 \times 10^5$</td>
<td>–</td>
</tr>
</tbody>
</table>
The performance of the filter, the influent turbidity was increased to approximately 40 NTU. All the other conditions were similar to Run 1.

The filters were cleaned after the first run. During cleaning, the standing water below the diffuser plate on the top of the sand bed was displaced, and the top 5 cm layer of sand bed was scrapped off manually. A few litres of clean water were poured on top of the sand bed in the filter and the filter top was again cleaned by agitating and rinsing the sand. This water was scooped off with a small cup and discarded. This was repeated four times until the water was clear. A 5 cm layer of fresh fine sand of the same specifications was placed on the top of the filter. The cleaned filter was flushed for a day following this.

Analyses

Influent and effluent samples were analysed daily/biweekly for different physico-chemical and bacteriological water quality parameters. Samples were also collected from different intermediate depths of the filter and dissolved oxygen concentration was checked. Concentrations of total coliforms and faecal coliforms were determined by using the multiple tube technique (most probable number – MPN method). Enumeration of heterotrophic bacteria was done by the plate count method using nutrient agar. Various physico-chemical parameters such as pH (Hanna pH meter (209)), turbidity (HACH 2100P)), total iron (phenanthroline method with Varian 50), nitrates (Brucine sulphate method) and ammonia were analysed in the laboratory. All the analyses were conducted as per Standard Methods (1998).

RESULTS AND DISCUSSION

Filtration rate

Figure 1(a) shows the changes in initial filtration rate each day in the three filters. Flow rate was determined based on the time to collect one litre of filtered water at the beginning of each feed. In Run 1, the average flow rates for all the three filters were similar in the beginning and gradually decreased as the run progressed. The decline in flow rate was expected due to filter maturation and particle accumulation. Since all the filters were charged with the same quantity and quality of water, they were expected to have similar head loss development. However the flow rate decreased more rapidly in the modified filters in both runs. In Run 1, the initial flow rates of the BSF (nail) and the BSF (scrap) were 0.32 L/min and 0.35 L/min respectively, which were decreased to 0.16 L/min and 0.20 L/min respectively, at the end of Run 1. The flow rate of the conventional BSF declined from 0.32 L/min to 0.27 L/min during the same period. The plausible reason for this could be that in modified filters, the corroded particles of ZVI might have filled the pores of the sand particles, thereby increasing the head loss in these filters. The flow rates in all the three filters increased substantially following the cleaning.

Turbidity removal

Influent and effluent turbidities for the two filter runs are presented in Figure 1(b). The average influent turbidities were 22 and 41 NTU in Run 1 and Run 2, respectively, for all the filters. Significant differences were not observed
between the mean effluent turbidities of the three filters in the two runs. During Run 1, the average effluent turbidity from the BSF was 1.07 NTU while turbidities from BSF (nail) and BSF (scrap) were 1.02 and 1.03 NTU, respectively. During Run 2, the average effluent turbidities of BSF, BSF (nail), BSF (scrap) were 0.90, 0.86 and 0.80 NTU respectively. Average turbidity removal efficiencies for the three filters from the influent were around 95% during Run 1 and 98% during Run 2, respectively. The results thus suggest that the modified filters did not show any improvement in terms of turbidity removal, and the effluent turbidity levels were not influenced by the influent values for the turbidity range tested in the study (17.0–45.4 NTU).

**Dissolved oxygen level**

Influent and effluent dissolved oxygen (DO) concentrations were monitored daily throughout the two runs. Passage of water through the filters resulted in reduction of DO in all the filters. The mean influent DO value in Run 1 was around 6.3 mg/L. The decline was, in general, higher in the modified BSFs compared with the unmodified BSF. The average effluent DO was 5.6 mg/L in the case of the BSF, while in the two modified BSFs these were 5.1 and 3.9 mg/L respectively for BSF (nail) and BSF (scrap). Thus, it is clear that the decline in DO is comparatively greater in BSF (scrap). This could be due to the DO consumption during the nitrate removal process (Westerhoff & James 2003). Another possible explanation could be that the metallic iron was modified or precipitated to other forms in the presence of oxygen, which might also cause reduction in DO levels in modified filters. It also indicates the different removal mechanisms and reactions taking place in the filters. It may be noted that the effluent DO in any of the filters during the filter runs did not fall below 3.0 mg/L, indicating that filters were always under aerobic conditions. In order to further analyse the DO variations across the filter bed, samples were taken from different depths of the filters during both the runs just before charging the filters. The DO concentrations of different depths taken on day 60 of Run 1 are presented in Figure 2. It is clear that the DO levels were lower at deeper layers of the filter. It is known that different biochemical reactions, including oxidation of organic matter, take place in the filter (Murphy et al. 2010).

**Nitrate removal**

In Run 1 the influent was spiked with an average nitrate concentration of 26.0 mg/L. In all the three filters, NO$_3$ concentration decreased in the effluents. As can be seen from Figure 3, among the three filters, the BSF showed the lowest nitrate removal while the BSF (scrap) showed the highest removal. Nakhla & Farooq (2003) reported simultaneous nitrification and denitrification occurring in slow sand filters. They reported that the denitrification efficiency in the filters was much more stable than the nitrification.
efficiency over time. Murphy et al. (2010) reported that during filtration, nitrification occurred in the upper aerobic layers of the BSF. It followed denitrification, which could reduce NO$_3^-$ concentration in the filtrates. While dissolved oxygen was present throughout the depth in the BSF, it is possible that denitrification occurred deep in the biofilm where there could be anoxic conditions. However, in the present study, since the ammonia in the influent was negligible, nitrification was not expected in the filter.

In the modified BSFs, nitrate removal was significantly higher compared with unmodified filters, with BSF (nail) and BSF (scrap) giving 58.5% and 88.56% removals, respectively. Nitrate removal mechanisms in the modified BSFs are complex since they contain ZVI. In addition to biological denitrification described above, the mechanism involves physico-chemical processes. Fe$^0$ can act as an electron donor for nitrate reduction with the electrons required to reduce nitrate coming from Fe$^0$ through the corrosion products, Fe$^{2+}$ and hydrogen (Hao et al. 2005). Studies have shown that the final products of chemical reduction of nitrate by ZVI are N$_2$ and NH$_4^+$ (Westerhoff & James 2003). According to Westerhoff & James (2003), nitrate removal is accompanied by ammonium production, proton and DO consumption. This is supported by the fact that the BSF (scrap) effluent showed comparatively high ammonia (average 0.2 mg/L versus negligible in the BSF (nail)), high pH and low DO. While the average influent pH was 8.02, effluent pH in BSF, BSF (nail) and BSF (scrap) was 7.84, 8.03 and 8.25, respectively. Chen et al. (2005) reported that the reduction of nitrate using ZVI was mainly diffusion controlled where mixing is important to achieve effective nitrate reduction. Since there was no mixing in the filters, nitrate reduction was not complete in the present study. Influent and effluent nitrogen could not be balanced in the present study. This could be explained on the basis of unmonitored nitrogen species such as N$_2$ and N$_2$O (Westerhoff & James 2005). Further detailed investigations are required to delineate the nitrogen removal mechanism by ZVI-modified filters.

Total iron

Total iron content in the influent and effluent were monitored during the two runs to verify if there was any leaching of iron from the modified filters. The results showed that the effluent total iron content was well below the permissible limit (0.3 mg/L) in the three filters throughout the operation. This is contradictory to the observation of Westerhoff & James (2003), who reported up to 6 mg/L of iron in the effluent from iron columns treating nitrates. This can be explained by the fact that in the present study iron filings were used only for a height of 15 cm in the top layer while Westerhoff & James (2005) used a completely packed ZVI column. Thus, in the present study, iron that is leached appears to have been removed by precipitation by the subsequent bottom layers of the sand.

Microbial removal

Reduction in bacterial concentration during the two runs in the three filters is presented in Figure 4(a). The trend in all three filters was towards increased total coliform reductions with increasing days of filter operation. This could be not only due to the maturation of the biofilm in the filters, but also due to the reduced filtration rate. In order to examine whether any relationship existed between bacterial quality and flow rate, effluent bacterial concentrations were plotted against flow rate for the three filters (Figure 4(b)). It is evident that for all the three filters, reduced flow rate resulted in increased total and faecal coliform removals. The trend, however, was more pronounced in the case of the BSF compared with the modified BSFs.

The microbial removal was always higher in the modified BSFs compared with the BSF by at least 1 log unit. Figure 4(a) shows that the average performance of the two ZVI-modified BSFs was similar. Up to 4 log total coliform removals were obtained in these filters. The heterotrophic bacterial count (HPC), enumerated during Run 1 and presented in Figure 4(a), shows that HPC reduction was higher in the modified biosand filters with an average of ~2 log removal, whereas it was only ~1 log removal in the BSF.

The improved microbial removal in the modified filters was expected due to the corrosion of metallic iron in the porous media (Noubactep et al. 2012). Iron corrosion results in volumetric expansion of the original iron particles. The formed oxides go through more voluminous intermediate stages of hydroxides, which are colloidal and very adsorptive in nature. It is expected that during these events, microbes are enmeshed in the mass of precipitating oxides...
and hydroxides as well as being adsorbed on to the surface of these precipitates (Noubactep et al. 2012). Hence, adsorption and co-precipitation could be the principal reasons for enhanced microbial inactivation in the ZVI-modified filters.

It may be noted that in the present study, after the first run, the filters were cleaned by scraping the top 5 cm of the sand layer and replenishing it with new sand. In the second run, the influent turbidity was increased from ~20 NTU to ~40 NTU. It is seen that increased influent turbidity and cleaning did not adversely impact the microbial removal capacity of any of the filters.

**CONCLUSIONS**

Results of the long-duration study showed that introduction of ZVI in the BSF resulted in significant improvement in bacterial removal. Modified BSFs showed improved performance by at least 1 log unit. Turbidity removal was not affected by the modification, and increased influent turbidity did not affect filter performance. Effluent turbidity remained below 1.0 NTU throughout the filter operation. Filtration through modified BSFs did not adversely affect the physico-chemical quality of the treated water, with iron concentration remaining within the drinking-water quality standards. ZVI-modified filters showed improved performance in nitrate removal particularly with use of iron filings.

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