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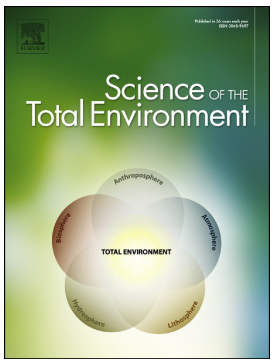

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A low-cost graphitized sand filter to deliver MC-LR-free potable water: Water treatment plants and household perspective

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Abstract

Scale-up feasibility of the graphitized sand filter (GS1) for Microcystin-LR (MC-LR) removal and its impact on other water pollutants (WPs) was assessed through a mass-balance study, using a laboratory-based drinking water treatment plant (DWTP) micromodel named: SAP-1©. The treatment system comprised: raw water tank, pre-oxidation tank (oxidant: potassium permanganate), followed by a coagulation/flocculation tank (alum supplemented), sedimentation tank, filtration module and finally disinfection tank (dosed with hypochlorite solution). Two filter modules (FMs) were studied: a) FM1: graphitized-sand media + sand media = ½ GS1 + ½ sand and b) FM2: ½ sand + ½ sand. The MC-LR removal study (initial concentration: 50 µg/L) was performed for two varieties of MC-LR source: a) commercial MC-LR, and b) algal-biomass released MC-LR. Along with MC-LR, other WPs were also evaluated including metal ions (Fe^{2+}

and Cu^{2+}), total coliform, turbidity, ammonia-N and dissolved organic carbon. The removal efficiency of these WPs was determined for each treatment unit (as it passed). FM1 was able to reduce the inflow residual of MC-LR (coming from the preceding unit: sedimentation unit) from 12.1 µg/L and 25.4 µg/L (for commercial and algal-cell MC-LR source, respectively) to < 0.61 µg/L and hence successfully complying the WHO guidelines (< 1 µg/L). The protein phosphatase 1A (PP1A) toxicity assay confirmed a much safer and more toxic-free filtrate (by 40%-50%) for FM1 as compared to the filtrate obtained from FM2. The techno-economic evaluation showed that for an annual household filter application, 160 CAD needs to be spent on one GS1-based filter unit as compared to over 6000 CAD (equivalent price) for the conventional sand-based filter to provide MC-LR-free water. The present study demonstrates the feasibility of the utilization of these units in household filtration systems.

Keywords: Water pollutant , microcystin, low-cost filter, treatment chain, drinking water, adsorption

1. Introduction

Microcystin-LR (MC-LR) is the most prominent cyanotoxin which is commonly found in the cyano bloom-affected aquatic ecosystems, polluting the drinking water sources, such as lakes, rivers and ponds. The WHO guidelines for MC-LR micropollutant in drinking water is < 1 µg/L (WHO, 2009). Hence, it is essential to treat the MC-LR-laden source water in a drinking water treatment plant (DWTPs) or by using household filters that directly filtrates source water. Apart from the aquatic organisms, MC-LR has a profound impact on human health too. MC-LR is a hepatotoxin and attacks the liver cells causing acute to chronic health effects, also damaging the immune system, kidney and sometimes leads to multiple organ failure too (Welten et al. 2019).

Most of the commonly practiced treatment methods in DWTP have shown effective MC-LR removal. The oxidation processes, such as ozonation and chlorination have even shown complete MC-LR removal at the laboratory scale (Lawton et al. 1999; Keijola et al. 1988). However, the oxidant dose is highly dependent on the MC-LR concentration to be treated along with other parameters such as pH, natural organic matter, and presence of other contaminants in the source water (Ma et al. 2012). Hence, a high MC-LR concentration demands higher oxidant dosage which results in toxic by-products formation in the treated water matrix after the latter complexes with the hydrolyzed or fragmented MC-LR molecules (Sovadiinova et al. 2017; Duan et al. 2018). Moreover, a longer contact time than normal is required to achieve complete removal of the MC-LR. Hence, to keep the dose under regulation limit and toxicity of the treated water under check, along with a need to follow strict operational residence time, the treatment unit should be less chemical-dependent, less energy-intensive and more economical. One such treatment unit is the sand filter. The main advantage of using a sand filter is that it is not an energy-intensive treatment process. It requires no chemical additives and is economical too. However, non- bioaugmented sand-based filters have resulted in poor MC-LR adsorption (< 20% adsorption capacity) (Kumar et al. 2020a). In contrast, many studies have also shown successful bio-sand filter operation for the MC-LR removal using bioaugmentation (Ho et al. 2006, Ho et al. 2007, Somdee et al. 2013). Most of these studies were performed at the bench-scale, which does not necessarily mean to show the same result at a higher scale knowing the complexity involved in a biological process. Moreover, bioaugmentation involves at least 2-3 weeks for a mature biofilm layer formation (under recirculation mode) and can pose a psychological stigma when the filter adsorbent is used in a filter for household applications (drinking and cooking).

A promising result from our previous study (Kumar et al. 2020b), obtained at the bench-scale using graphitized-sand adsorbent for various water pollutants including MC-LR (> 90% removal) prompted the team to further check the adsorbent feasibility at a higher scale (from 110-gram GS1 adsorbent to ~ 1700 gram). The graphitization of sand was performed using a sustainable sugar solution in the form of brewery waste effluent. This study not only highlights the importance of graphitized-sand filter in the treatment chain of a DWTP as compared to sand-based filter, but also provides a glimpse of its potential application as a stand-alone household filter. The techno-economic feasibility study for GS1 adsorbent as a household filter is performed according to the model guidelines as defined by the center for affordable water and sanitation technology (CAWST) (cawst.org).

During the plant operation, it is important to understand the mass balance of contaminants that defines the water quality at each treatment stage. These include primary water pollutants (WPs), such as metals (copper, iron), dissolved organic matter, turbidity, total coliform, ammonia-N. Most of the successful studies based on the removal of one or more water pollutants are only specific to a particular treatment unit or process. Such a research approach needs to be further explored in form of retrofitting these successful treatment units into an actual treatment chain (prototype approach) to provide information on the impact of such treatment units in the existing treatment pattern. Herein, in this study, a mass balance approach is presented for the above mentioned WPs including MC-LR using two different sources (commercial as well as algal cells-derived). GS1 filter is retrofitted in the existing DWTP treatment chain (micromodel scale) to better understand its role, responsibility and impact in an overall removal of MC-LR and other WPs. The benefit of mass balance study includes progressive treatment know-how of a particular WP and hence the treatment objectives can be customized based on the change in the

influent/effluent parameter expected in the previous unit in the existing chain. Moreover, a mass balance study can further be used to decipher the actual treatment efficiency using the modified treatment chain by the addition of any new/retrofitted treatment unit/s.

To the best of our knowledge, it is the first time a mass balance approach is studied to report various water quality parameters (WQPs) using a laboratory-made DWTP micromodel that includes MC-LR. Also, for the first time, a treatment comparison has been made using two distinct sources of MC-LR: commercial and algal-cells derived MC-LR. The set-up is fully automatic which was modeled to treat 2 liters of lake water as per the similar residence/treatment time involved in the real treatment module of a typical DWTP. This study also comprises a toxicity assessment of the filtrate water derived from both filter modules to ensure toxic-free deliverance for the drinking water consumers. Towards the end, a preliminary techno-economic study of the standalone graphitized-sand filter was performed to check its feasibility for the household purpose.

2. Material and methods

This section and the follow-up discussion comprises experimental methodologies and are sequenced and streamlined as follows: a) Introduction of the micromodel DWTP treatment chains (conventional and modified), b) analysis of MC-LR and various WPs for both treatment chains, c) Impact of GS1 filter in DWTP chain and d) Preliminary techno-economic study of standalone GS1 filter and sand filter for household perspective.

2.1 Reactor fabrication, chemicals and reagents

Plexiglass column reactors were fabricated by Poly Alto, Quebec City, Canada, dimensioning 9 cm x 9 cm x 33 cm with a thickness of 8 mm from all sides. These columns were used to

construct the filters. A compact digital mixer system was bought from Cole-Parmer (Ontario, Canada) to stir the coagulant at a defined vortex gradient speed. Water Quality Parameter (WQP) kit for Cu^{2+}, Fe^{2+} and ammonia-N, aerator pumps, pipelines, check valves, barbed connectors, fitters and other accessories were bought from Amazon.ca, Canada. The oxidants: potassium permanganate and alum: aluminum sulphate, were bought from Sigma Aldrich, (Ontario, Canada). For the PP1A assay, enzyme and substrate: Protein Phosphatase-1 Catalytic Subunit (α-Isoform from rabbit) and p-nitrophenyl phosphate (pNPP), respectively, were purchased from Sigma Aldrich (Ontario, Canada). Quartz sand used as the filter media was obtained from Chemin Ste-Foy DWTP, Quebec City, Canada.

2.2 Preparation of lake water

Lake Sainte-Anne (47.262879N, -71.665158W) water was used as an influent matrix solution termed as 'raw water'.The contaminants were spiked to reach the final concentration as follows: NH_4-N: 5 mg/L, Cu^{2+}: 20 mg/L, Fe^{2+} 10 mg/L, MC-LR: 50 µg/L (both commercial as well as one released from laboratory-cultured algal biomass). Before spiking the above contaminants, the background concentration of each pollutant was determined and then accordingly, the final solution was prepared.

API® freshwater master test kit-800 was used for ammonia-N, Cu^{2+} and Fe^{2+} calibration and sample analysis experiments. The color produced by the reagents and sample test volume was calibrated spectrophotometrically where absorbance was measured at the characteristic wavelength ($\lambda_{max,NH4\text{-}N}$ = 690 nm, $\lambda_{max,Cu2+}$ = 610 nm; $\lambda_{max,Fe2+}$ = 585 nm) as obtained from the scan kinetics results using UV Cary 300 spectrophotometer instrument. Ammonium sulphate was used as the ammonia-N source and was spiked in the lake water according to the stoichiometric calculations, to prepare a final concentration of 5 mg/L NH_4^+-N (final volume: 2 liter).

Dissolved organic carbon (DOC) was estimated using Shimadzu 5000A analyzer (Shimadzu, Japan). In brief, around 50 mL of the effluent sample was filtered using a 0.45 µm glass-fiber filter and analyzed for the DOC. The average DOC in lake water sample was 4.1 ± 0.6 mg/L which was further increased to 14.8 ± 1.1 mg/L using dextrose (relationship of dextrose dose and DOC is mentioned in the supplementary section). In general, DOC in lake water remains < 6 mg/L but in this study, DOC level was enhanced to represent the source water during peak rainy season (worst case).Total coliform was determined by the membrane filtration technique according to the standard method APHA (1998). The average total coliform in lake water was reported to be 121 ± 37 CFU/100 mL.

Fe^{2+} and Cu^{2+} metal ions were chosen as the metal ion indicator in lake water where $FeSO_4.7H_2O$ and $CuSO_4.5H_2O$ were used as the respective metal source. The initial Fe^{2+} and Cu^{2+} concentration of 10 mg/L and 20 mg/L was chosen based on the stoichiometric equivalent of the metal sources (as mentioned above) and measurement was done spectrophotometrically. The background concentration of ammonia-N and Cu^{2+} in lake water ranged 0.1-0.3 mg/L and 1.3-2.3 mg/L and thus the final prepared raw water recipe containing a copper concentration of 20 mg/L (spiked) did not form an ammonia-Cu complex in a significant amount and vice-versa. Thus, only for ammonia-N analysis (for initial concentration: 5 mg/L), it was made sure that the raw water (prepared lake water) does not contain spiked copper ions and vice-versa as otherwise, it could have interfered in the colorimetric analysis. Hence, two separate lake water influent were prepared where the second batch was used every day only for the analysis of Cu^{2+}/NH_4-N to ensure better and near accurate quality control of the sample analysis.

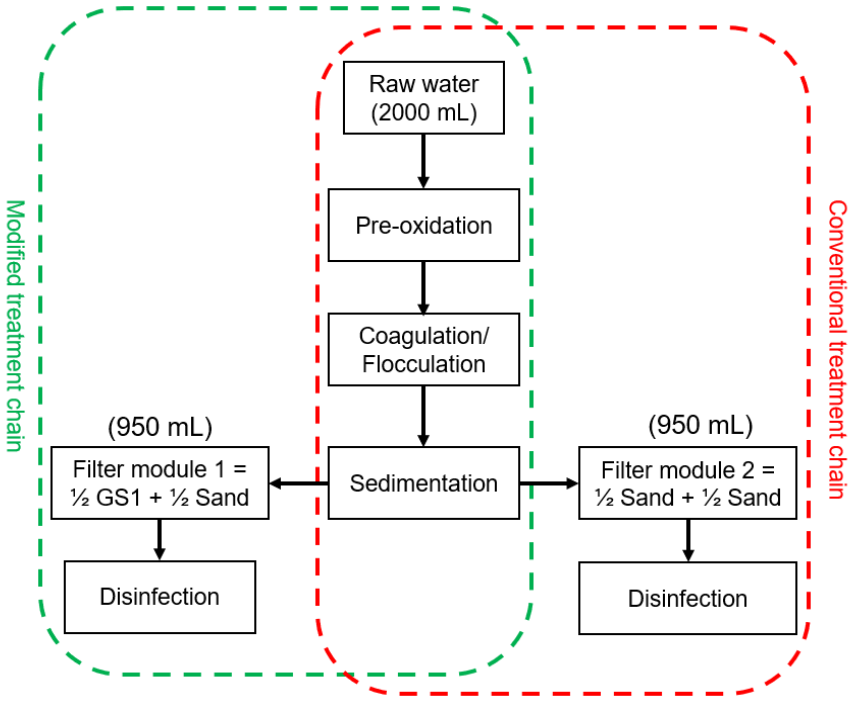

Figure 1: Flowchart of the treatment chain for both the filter modules; GS1: Graphitized sand

Finally, the turbidity of the prepared lake water was measured using HACH instruments 2100A which averaged 42.5 ± 5.2 NTU. Figure 1 shows the flowchart diagram of the treatment chain being studied in the current study where filter module 1 comprised graphitized-sand filter (as half filter plus a sand filter as another half), while filter module 2 comprised only sand filter representing modified and conventional treatment chain, respectively. Turbidity, total coliform, Fe^{2+} and Cu^{2+} analysis was done each day for 41-days experiment while NH_4-N, DOC and MC-LR (both sources) were done 16 times (once every 2-3 days), 6 times (once every 6 days) and 5 times (once every 8 days) for a total of 41 days, respectively.

2.3 DWTP model SAP-1© set-up

A DWTP micromodel was set-up in the comprising raw water tank, pre-oxidation, coagulation/flocculation, sedimentation, filtration module, and disinfection treatment unit. Two

filter modules were studied viz. sand filter module (½ sand + ½ sand: control) representing the existing DWTP treatment chain whereas a hybrid filter module (½ GS1 + ½ Sand) to understand the impact of the graphitized sand module in a 'modified' DWTP treatment chain (here only filter module 1 is shown = ½ GS1 + ½ Sand). Figure 2 shows the set-up model representing a typical DWTP, named as SAP-1©. Filters consisted of sand/graphitized sand (GS) media (depending on FM1/FM2) 22 cm in height followed by the drainage section (particles size >2 mm and <5 mm). Graphitized sand was synthesized using brewery effluent liquid containing sugar as detailed in our previous study (Kumar et al. 2020b). The effective diameter of the filter grain in filters was around 0.26 mm with a coefficient of uniformity <2.4. The raw water tank was filled with 2L lake water (preparation as discussed above) and the feed influent was immediately transferred to the pre-oxidation tank using an auto-dosage pump where potassium permanganate was used as an oxidant (dose: 1.5 mg/L). After 10 minutes of pre-oxidation (aerated continuously using air pump), the treated water was pumped into the next treatment unit: flocculation tank, where alum (90 mg) was dosed for the oxidized raw water. The treated water was stirred at 225 ppm for 2 minutes (to allow a uniform dispersion of alum) followed by slow stirring at 50 rpm (flocculation) for 10 minutes.

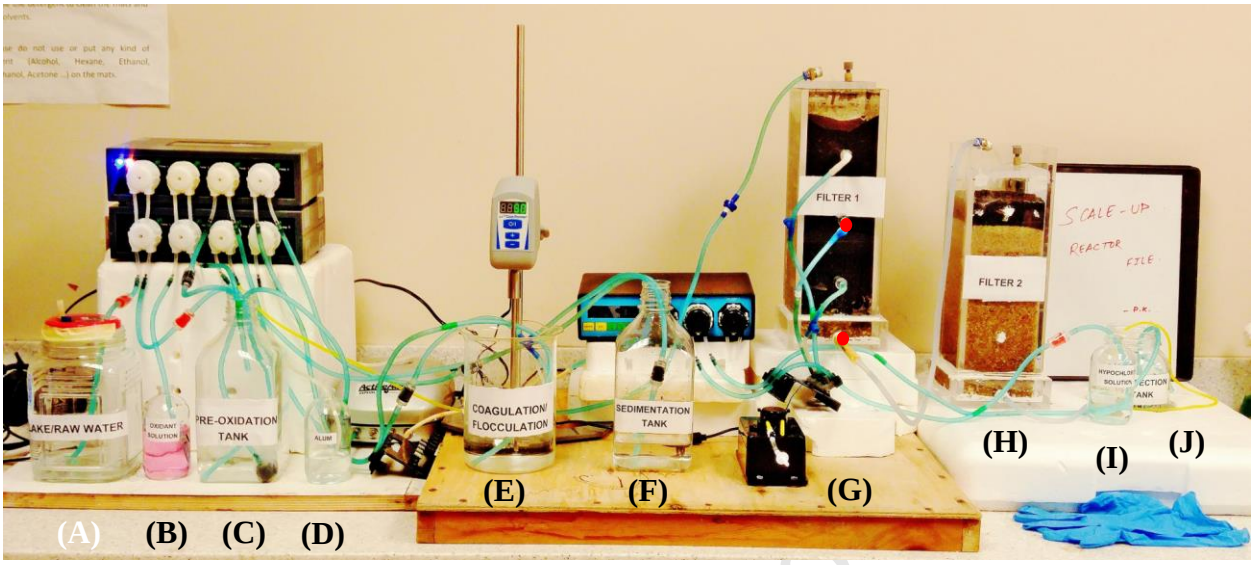

Figure 2: Drinking water treatment plant micro-model (SAP-1©); the red dot shows the mid and end sampling port of the GS1 filter; GS1: Graphitized sand; Letters A to J has been detailed in Table 1

The supernatant (around 1.95 liters) was discharged to the sedimentation tank allowing a settling time of 45 minutes (typically expected in a real sedimentation tank present in DWTPs). Afterward, the supernatant (1.95 L) was pumped to both filter modules equally (950 ml each) which filtered water at an overall rate of 100 ml per minute (0.75 m/h). The filter rate was measured at the effluent port that opened to the disinfection unit. The disinfection unit was dosed with 4 drops or 0.15 ml @ 6% hypochlorite solution (bleach) for approx. 0.9 liter of filtered water for each filter module separately (as shown in Figure 1).

The disinfection tank was aerated for 1 minute to mix the hypochlorite and then left undisturbed for 5 minutes to complete the process. Table 1 shows the treatment chain unit with their residence time, chemicals used and their respective dosage. The transfer of influent/effluent between two treatment units was performed through the auto-dose pump (as shown in Figure 2), set at a defined run time according to the residence time of the influent as described in Table 1. Overall, the process took 110 minutes starting from the raw water tank to the disinfection tank.

Before commencing the actual study, the set-up was run for 3 days with each day, 6 liters of lake water treated before starting the 41-days WQPs testing and analysis. This was performed to adjust the influent-effluent conditions in the set-up chain and calibrating the auto-dosage pump with precision. In total, 8 pump channels were used to make the operation fully automatic and convenient for the operator.

Table 1: Treatment module details and characteristics

Name	Treatment unit	Residence time (min)	Chemical added (if any)	Remarks
A	Raw water/Lake water tank	0	NA	NA
B	Oxidant solution	NA	Potassium permanganate	Stock solution of PP: 60 ppm, dose vol.: 50 mL.
C	Pre-oxidation tank	10 min	Oxygen bubble (aeration)	Final dose: 1.5 ppm
D	Alum	NA	Alum	Stock solution of PP: 1125 ppm, dose vol.: 80 mL.
E	Coagulation/Flocculation	10 min	Alum	Final dose: 45 ppm
F	Sedimentation tank	45 min	NA	NA
G	Filter 1 (GS1 filter for FM1 and sand filter for FM2)	10 min	NA	Main filter
H	Filter 2 (Sand filter for FM1 and sand filter for FM2)	5 min	NA	Extension filter
I	Hypochlorite dose	NA	Bleach in our lab (6% NaOCl)	Stock sol of 8.25% hypochlorite sol., dose vol: 0.15 mL
J	Disinfection tank	6 min		NA

NA: not applicable; FM1 and FM2: Filter module 1 and 2; GS1: Graphitized sand; PP: Potassium permanganate

2.4. Justification for pre-oxidant and coagulant dose

2.4.1 Justification for potassium permanganate dose

Potassium permanganate (PP) has been widely used as the point-of-entry treatment for many years. One major advantage of using PP is that it oxidizes the metal contaminant and converts them into the oxide form which can be settled or filtered later and hence easy to remove from the polluted source water matrix. Also, it removes taste and odor problems even after it combines with the chlorine molecules later in the treatment. 1-1.5 ppm dose of PP for 10-15 minutes was

found suitable for the pre-oxidation purpose (Welch, 1963). Hidayah et al. (2018) tested a range of PP dose from 0.25 to 4 ppm and found major changes that happened in terms of disinfection by-product (DBPs) formation. The least DBPs formed at a dose of 1.8 ppm (reduced by 23% from peak value). Hence, for this study, a dose of 1.5 ppm was chosen for the treatment.

2.4.2 Study for alum coagulant dose

Iron-based coagulants are expensive as compared to alum (for a similar equivalent dose) and the former reduces the alkalinity of raw water which degrades the water quality too (Gebbie, 2006). Also, iron-based coagulants generate fluffier flocs that take time to settle. Hence, in this study, crystalline potassium aluminum sulphate, $KAl(SO_4)_2 \cdot 12H_2O$ was used to counter the above challenges. An Alum dose of 45 mg/L was selected based on the literature review of some studies using a jar test experiment (Ebeling et al. 2003, Kamel et al. 2018).

2.5 Toxicity analysis using protein phosphatases inhibitory assay (PP1A assay)

Protein phosphatase 1 (PP1) belongs to a protein serine/threonine phosphatases class and is related to the control of glycogen metabolism in the liver. Since MC-LR is a hepatotoxin, it inhibits the kinetic activity of PP1 protein. Many researchers have specified PP1A assay to report the toxicity of the MC-LR samples. In this study, PP1A assay was performed following a developed protocol for MC-LR by Moore et al. (2016) with some modifications.

This assay was performed in a 96-well plate. In a 300 µL well, 20 µL of the sample or known MC-LR (to prepare the standards), 40 µL of PP1 enzyme (well concentration of 0.85 U/mL), and 240 µL of pNPP substrate (final well concentration of 115 mM) were mixed to initiate the enzyme-substrate reaction. A blank was also prepared with a substrate blank (containing only substrate solution), which represented the baseline activity of PP1 to normalize the effect of MC-

LR in a PP1 activity. The PP1A activity rate was determined based on the optical density (OD) at λ_{max}: 405 nm after every 2 minutes for 1 hour. After 1080 seconds, the plateau region was reached for the substrate blank from where a change in OD/min was calculated, until 3480 seconds (not shown here). The more the hydrolysis of pNPP by PP1A enzyme, the lesser the OD observed and lesser the PP1A inhibition and hence more the PP1A activity. All measurements were done in triplicates.

2.6 Culture of *Microcystis aeruginosa* and MC-LR analysis

Microcystis aeruginosa was received as a kind gift from Dr. Jerome Compte (Professor, INRS-ETE, Quebec City, Canada) in a 30 ml culture tube. BG-11 media was used for culturing *M.aeruginosa* as mentioned by Rippka et al. (1979). A fluorescent lamp was installed to provide a constant source of light (8h/16h; light/dark phase) for the growing culture. Every week for up to 12 weeks, 10 ml of prepared BG-11 media was added to the growing culture in a 250 ml Erlenmeyer flask and optical density at λ_{max} = 700 nm was noted down (not shown here). After 12 weeks of culture growth, for up to 6 more weeks, MC-LR toxin was analyzed in the growing medium. For this, 3 ml of culture was filtered using a 0.45 μm HA filter where cells were retained over the filter and filtrate was further used for the MC-LR analysis (only extracellular MC-LR was analyzed). For the MC-LR analysis for the first 4 cycles (n=4), the samples were analyszed using PP1A enzymatic assay as described in our previous study (Kumar et al. 2020c) and for the 5^{th} and last cycle (due to unavailability of PP1A enzyme), the samples were analyzed using ultra-high-performance liquid chromatography (uHPLC) method adapted from Roy-Lachapelle et al. (2019).

The limit of quantification (LOQ) was set at the lowest concentration level of the calibration curve (i.e. 0.1 μg/L). At the end of 6-weeks of MC-LR analysis, a final mean concentration of

2500 μg/L was obtained from a 150 ml culture that was sufficient to prepare 2-liter lake water at a final MC-LR concentration of 50 μg/L using dilution for more than 10 times or instances.

2.7 Techno-Economic Analysis

A basic techno-economic analysis was performed for the sand and GS1 household filter unit according to the CAWST biofilter version 10.0. The volume and mass of adsorbent material (sand or graphitized sand) were determined according to the bulk density of each material. The information on the cost of sand (per tonne) was obtained from the DWTP operator, Mr. Guy Grosielliers (Chemin Ste-Foy, Quebec City, Canada). The coating solution in case of GS1 is brewery waste effluent (hop-free) that is assumed to be collected free of cost (kind contribution) from the nearest brewery shop where the material synthesis will be done. Only the nominal transportation cost was included that will vary owing to the proximity of the material synthesis site and brewery shop. However, the transportation cost is assumed to be subjective and insignificant as compared to the overall filter cost when prepared in bulk. Cost of fittings, concrete mix and other accessories was assumed to be $100 per filter which can be further reduced if manufactured in bulk. Other information such as labor cost, capital cost (including muffle furnace), electricity cost, number of labor needed, etc. is tabulated under Table 3. The technical parameters are discussed more in detail in section 4. All the calculations were performed in the excel sheet.

2.8 Statistical Analysis and graphics

All statistical analyses comprising standard deviation, average, student t-test, p-value comparison, Principal Component Analysis (PCA) and all graphical presentations were performed in ORIGIN software (Version 8.5; OriginLab).

3. Results and discussion

3.1 Microcystin-LR removal

Initial MC-LR concentration for the commercial (MC1) and one extracted from algal cells cultured in the laboratory (MC2) were kept nearly the same at 50 µg/L and 56.8 µg/L in the prepared lake water influent. It was difficult to anticipate before the extraction process, the amount of dilution required for the MC-LR extracted from the algal cells to reach a target concentration of 50 µg/L, as cells continue to produce toxins offsetting the rise between two sets of analysis. Hence, the starting MC-LR concentration was obtained slightly greater than 50 µg/L. It was observed that the MC1 removal was more than MC2 after pre-oxidation (Table 2). However, coagulation and sedimentation treatment modules kept the degree of MC1 and MC2 removal almost similar. A major change was observed after filtration from filter module 1, where the residual MC1 and MC2 coming from the sedimentation tank, 12.1 ± 0.9 µg/L and 25.4 ± 1.2 µg/L, respectively, further decreased the MC-LR concentration to < 0.6 µg/L (both cases) complying WHO guidelines (< 1.0 µg/L). This attributed to the remarkable adsorption capacity of graphene-sugar sand (GS1) which was capable to adsorb high concentration of the MC-LR present in the influent raw water.

To further test the adsorbent strength of GS1, 50 µg/L of MC1 and MC2 were directly fed to GS1 filter block (1/2 GS1 filter of filter module 1) and checked for its filtrate concentration from mid-port as well as the end port (shown in Figure 2 by the red dot), before it enters the other half filter of the same module (i.e., ½ sand filter). Complete removal of MC-LR (~ 0.6 µg/L) was observed from both the ports which might suggest that $1/4^{th}$ GS1 filter was enough to remove a high degree of MC-LR (50 µg/L). Though, this concentration is rarely found in any natural water bodies, except the peak cyanobloom season. However, these results need to be further verified in

terms of longevity of the filters as the current study only reported five runs of MC-LR at regular intervals of a 41-day experiment (five each for commercial and algal cell-derived MC-LR). However, from our previous study on graphitized sand filter adsorbent at the bench scale (110 gram), a 16-week operation of the filter (3 times water discharge per day @ 50 μg/L: 40 mL each), did not show any breakthrough of MC-LR in the filtered water. This particular experimental fact was utilized to calculate the nominal MC-LR adsorption capacity of the GS1 material during the techno-economic analysis (discussed in section 4).

3.2 MC-LR toxicity assessment of filtrate from both filter modules

Figure 3 (A) and Figure 3 (B) shows the bar chart of the PP1A activity (%) assay for filter module 1 and filter module 2, respectively. Each week, the assay was performed five times (n=5) for the filtrate obtained from both the modules. The final PP1A % activity was reported as the mean of all the weekly values (5 times a week for 5 weeks = 25 observations). A higher PP1A activity was obtained for the filtrate sample obtained from FM1 (71.4 ± 2.9 % and 66.2 ± 4.2 %, calculated as the mean of the means) as compared to FM2 (29.2 ± 1.5 % and 15.9 ± 2.4 %) for commercial MC-LR as well as algal cells-derived MC-LR. Also, the PP1A activity of the filtrate obtained for commercial MC-LR (red bar) was significantly higher than the algal cells-derived MC-LR (green bar) for both the filter modules which were tested individually. The p-value for FM1 observations was 0.09 as compared to the p-value of 0.003 for FM2 filtrate. Overall, it strengthens the fact that graphitized sand filter media is better than sand media for providing safe and drinkable water free of MC-LR and its toxic by-products.

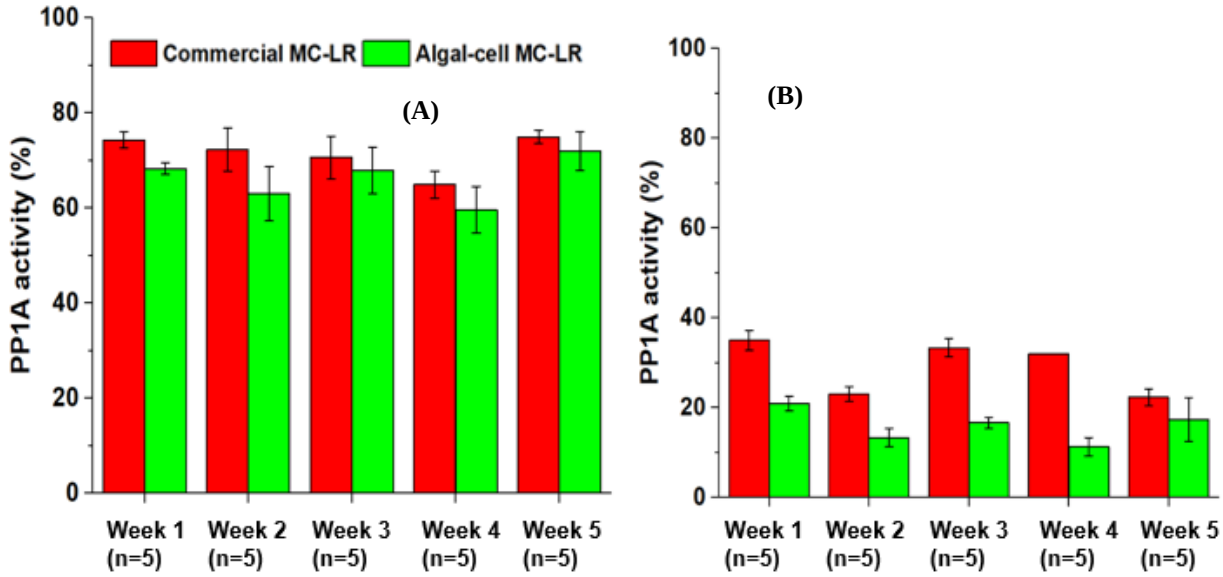

Figure 3: PP1A % activity of the filtered sample from (A) Filter Module 1 (½ GS1 + ½ sand) and (B) Filter module 2 (½ sand + ½ sand); GS1: Graphitized sand; PP1A: Protein phosphatase 1A. (Readers are advised to refer the online version of the article to see the color mapping)

For both filter modules, algal-cell derived MC-LR showed more relative toxicity as compared to the commercial MC-LR. As a comparison, blank showed an activity of 87 ± 5 %. This shows that though filter module 1 attained a complete MC-LR removal with over 70% and over 65% of PP1A activity, tested using commercial and algal-cells derived MC-LR, respectively, a fair amount of toxicity persisted in the filtered water. However, a better inference can only be made to the final toxicity by obtaining a degradation mechanism pathway of the filtered sample to report for molecules or fragments containing adda moiety (responsible for toxicity in MC-LR degraded sample) (Campos et al. 2010). In this study, no separate sub-study was done to explore the MC-LR by-products or its degradation mechanism. However, this conclusion can be taken with two possibilities: a) 15-20% less PP1A activity shown by filtrate of FM1 as compared to the control could be due to the presence of other water pollutants along with MC-LR or b) a need for bioaugmentation of filter which can form a research gap (biofilter concept) to this study and can

be studied in future to report if the PP1A activity of the filtrate reaches a value close to the control. Many studies on bacterial degradation of MC-LR explored for the reduced toxicity in the treated water where bacterial strain showed the presence *mlrA* gene that was mainly responsible for reducing the toxicity of the MC-LR (by up to 200 times) (Bourne et al. 1996, Dziga et al. 2012).

3.3. Discussion on other water quality parameters

3.3.1 pH and Dissolved oxygen (DO) analysis

Figure 4 shows the trend of pH and DO in different treatment units of the set-up: SAP-1©. In total, pH and DO measurements were taken 7 times during the 41-day experiment. Initial raw water pH and DO were 7.12 ± 0.06 and 4.65 ± 0.1 mg-O_2/L, respectively. After pre-oxidation, the DO increased to 5.45 ± 0.21 mg-O_2/L as it was continuously aerated during the process, while pH remained almost the same (7.01 ± 0.16). The coagulation step further elevated the DO content of the influent water and could be due to the mixing process during the flocculation stage (Figure 4).

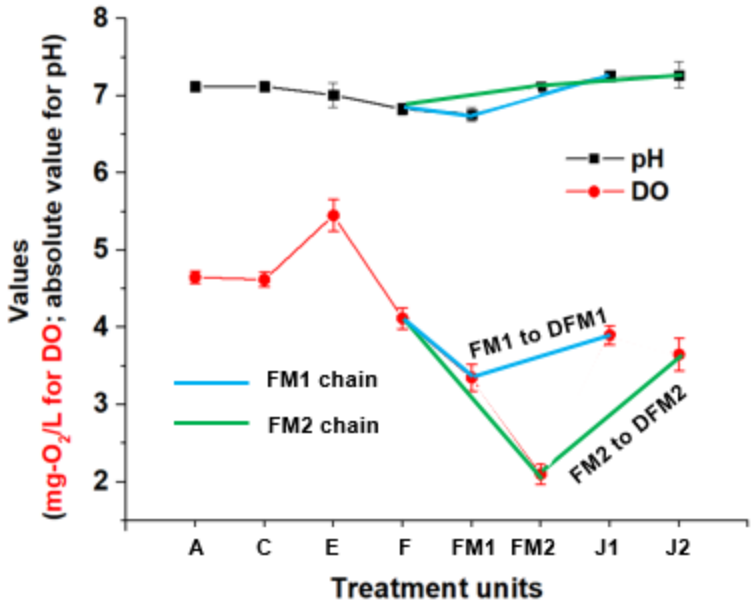

Figure 4: pH and Dissolved Oxygen (DO) trend in different treatment modules (x-axis); A: Raw water;C: Pre-oxidation tank; E: Coagulation/Flocculation; FM1: Filter module 1; FM2: Filter module 2; DFM1/DFM2 or J1/J2 disinfection tank of FM1/FM2. J1 and J2 denotes disinfection unit for modified treatment path and conventional treatment path, respectively as mentioned in Figure 1. (Readers are advised to refer the online version of the article to see the color mapping)

However, after the sedimentation step, DO decrease to 4.12 ± 0.14 mg-O_2/L from 5.45 ± 0.21 mg-O_2/L which could be due to non-mixing conditions during the 45 min long-standing period. The pH of the influent water kept on decreasing and fell to its minimum value of 6.76 (0.36 lower than raw water) for FM1 module filtrate but remained the same for the filtrate obtained from FM2 (7.1 ± 0.1). Overall, the pH of the filtrate did not change by much perhaps due to the PP action as an oxidant (not reduced the alkalinity by a significant amount: just 0.36 change in pH value).

However, filter module 1 and filter module 2 mainly reduced the DO of the incoming water from the sedimentation tank, especially FM2 filtrate that showed an average DO of < 3 mg-O_2/L. This could be due to less dissolution of oxygen within the sand grains (of both ½ sand filters) as compared to filter module 1 that consists of graphitized sand where more diffusion of oxygen

happened due to larger pore volume as derived from the BET analysis (7.1 cm^3/g as compared to 3.2 cm^3/g for sand). Also, the pH of filtrate from FM1 was lower than (6.76 ± 0.2) the filtrate obtained from FM2 (7.1 ± 0.3). This could be due to more DOC removal by FM1, from 6.5 ± 0.2 to 1.88 ± 0.3 mg/L, as compared to FM2, from 6.5 ± 0.2 to 4.1 ± 0.4 mg/L (more details are provided in a later section). However, the consumption of DO by heterogenous/opportunistic bacteria present in lake water (and growing within the filter columns) in FM1 was found to be more effective in utilizing dissolved carbon than that of FM2 as the change in DO/mg-DOC removal for the latter was comparatively higher (0.83 mg-O_2 utilized/mg DOC removed) than the former (0.16 mg-O_2 utilized/mg DOC removed). This strengthens the fact that the population of heterogenous/opportunistic bacteria in graphitized sand grains (part of FM1) is relatively more productive than that attached over the sand grains in terms of organic carbon removal. Also, ammonia-N removal in FM1 (4.1 ± 0.3 to 1.1 ± 0.1) is comparatively higher than FM2 (4.1 ± 0.3 to 3.3 ± 0.4) and could be due to presence of more nitrifying bacteria attached over the GS1 adsorbent as compared to sand. Nitrification proceeds with a decrease in pH and consumption of oxygen (4.47 mg O2 per 1 mg of ammonia-N) and hence the presence of carbon utilizing bacteria and more active nitrifiers present in GS1 filter might be the reason for pH and DO relationship as discussed (Wezernak and Gannon, 1967). However, a long-term evaluation and genomic analysis of the formed biofilm could lead to a more definite conclusion on the relative abundance and identification of high carbon utilizing bacterial species.

3.3.2 Turbidity, total coliform, and Dissolved organic carbon (DOC)

Table 2 shows the data of water quality parameters tested for the treatment chain comprising two different filter modules. The initial turbidity of the raw water was 42.5 ± 5.2 NTU and can be attributed to high organic components (DOC: 15 mg/L) present in it along with the suspended

solids. This value represents season-peak turbidity of the lake water during the rainy or melting season when more organic compounds leach and mix with the surface water bodies. After pre-oxidation, the turbidity reduced to 32.2 ± 4.8 NTU, but a major change was observed after the coagulation step when turbidity reduced to 18 ± 3.2 NTU followed by settling of suspended particles in the sedimentation tank which further reduced it to 8.1 ± 2.3 NTU. After filtration (filter module 1), the turbidity dropped down to 0.6 ± 0.3 NTU which complies with the Canadian drinking water guidelines. On the other hand, it can be observed that filter module 2 still showed an average turbidity of 2.3 ± 0.9 NTU. Initial total coliform present in the raw water was 121 ± 37 CFU/100 mL and reduced drastically after pre-oxidation to 42 ± 16 CFU/100 mL. Filter 1 further reduced this count to 2 ± 1 CFU/100 mL and disinfection showed almost complete removal. Both the filter modules were found equally efficient in removing the total coliforms. Considering the utility of filter modules for a household purpose, both filters (FM1 and FM2) performed equally well, achieving an almost complete coliform removal.

Table 2: Water Quality Parameters along the treatment chain

Water Quality Parameters	**Raw water**	**Pre-oxidation**	**C/F**	**Sedimentation**	**½ GS1 + ½ Sand filter**	**Disinfection**
Turbidity (NTU)	42.5 ± 5.2	32.2 ± 4.8	18 ± 3.2	8.1 ± 2.3	0.6 ± 0.3	0.3 ± 0.1
					½ Sand + ½ Sand filter	**Disinfection**
					2.3 ± 0.9	1.5 ± 0.6
NH_4-N (mg/L)	5 ± NIL	4.6 ± 0.3	4.2 ± 0.4	4.1 ± 0.3	1.1 ± 0.1	ND
					½ Sand + ½ Sand filter	**Disinfection**
					3.3 ± 0.4	ND
MC-LR commercial (µg/L)	50 ± NIL	23.8 ± 2.3	13.2 ± 1.4	12.1 ± 0.9	< 0.1	<0.1
					½ Sand + ½ Sand filter	**Disinfection**
					8.2 ± 0.4	4.1 ± 1.1
MC-LR Algae	55.8 ± 1.2	45.9 ±	28.7 ± 2.7	25.2 ± 1.2	<0.1	<0.1

cell (µg/L)		1.7				
					½ Sand + ½ Sand filter	**Disinfection**
					20.9 ± 0.9	14.2 ± 1
DOC (mg/L)	14.8 ± 1.1	11.2 ± 1.5	8.3 ± 0.6	6.5 ± 0.2	1.8 ± 0.3	ND
					½ Sand + ½ Sand filter	**Disinfection**
					4.1 ± 0.4	ND
Fe^{2+} (mg/L)	10 ± NIL	7.95 ± 0.4	4.7 ± 0.55	3.1 ± 0.5	0.95 ± 0.4	ppt
					½ Sand + ½ Sand filter	**Disinfection**
					2.3 ± 0.4	ppt
Cu^{2+} (mg/L)	20 ± NIL	15.2 ± 1.1	13.4 ± 1.4	11.9 ± 1.2	2.6 ± 1.1	ppt
					½ Sand + ½ Sand filter	**Disinfection**
					6.6 ± 0.6	ppt
Total coliform (CFU/100 mL)	121 ± 37	42 ± 16	21 ± 7	24 ± 4	2 ± 1	1 ± 1
					½ Sand + ½ Sand filter	**Disinfection**
					3 ± 3	2 ± 1

Ppt: Precipitation formed in most of the analysis; CFU: Coliform forming unit; C/F: Coagulation/Flocculation; NTU: Nephelometric Turbidity unit; DOC: Dissolved Organic Carbon

Dissolved organic carbon present in raw water was 14.8 ± 1.1 mg/L, which after pre-oxidation was not removed and the value remained on a higher side (> 11 mg/L). The specific UV absorbance (SUVA) calculated for the raw water is 2.16 (< 3) and hence more hydrophilic compounds are expected to be present as compared to the hydrophobic compounds. In general, water with a less SUVA (< 3) shows less reactivity with the oxidizing compounds (here $KMnO_4$) (Fearing et al. 2004). Hence, it can be inferred that the raw water is composed of more hydrophilic compounds (HiM) and hence was difficult to be removed due to pre-oxidation by $KMnO_4$. Another study by Zhao et al. (2018) reported a similar observation where after $KMnO_4$ pre-oxidation, the HiM fraction of DOC just decreased by 0.2 mg/L from its initial concentration of 1.8 mg/L.

A major change occurred after the treatment from filter module 1, which reduced the DOC value of the supernatant coming from the sedimentation tank from 6.53 ± 0.2 mg/L to 1.89 ± 0.3 mg/L. After disinfection, the value reduced to a non-detection level. On the other hand, DOC still needed a better removal efficiency when filter module 2 was used. It is because high organic matter present during disinfection (here: 4.1 ± 0.4 mg/L) can combine with chlorine to form disinfection by-products (DBPs) such as THMs, dihaloacetic acids (DHAAs) and trihaloacetic acids (THAAs), especially for DOC level exceeding 4 mg/L (Bond et al. 2014). The formation of DBPs was not investigated in this study.

3.3.3 Ammonia-N removal

Initial ammonia-N present in raw water was 5 mg/L and its removal was noted for each treatment unit. Due to the high solubility of ammonia-N in water, there was hardly any change observed until the sedimentation unit (4.1 ± 0.3 mg/L). Even pre-oxidation did not remove the dissolved ammonia-N (Table 2). However, a maximum change was observed during filtration from filter module 1, where ammonia-N decreased from 4.1 ± 0.3 mg/L to 1.1 ± 0.1 mg/L. On the other hand, filter module 2 showed poor adsorption of ammonia-N as the filtrate showed 3.3 ± 0.4 mg/L of NH_4-N. The major change observed for filter 1 could be attributed to effective adsorption due to a high mesoporous surface of the graphitized sand as a BET isotherm of type IV was obtained (not shown here). A lower NH_4-N removal by FM 2 could have been increased by recirculating the effluent or by siphoning the 'top-layer' sand biofilm to regulate the autotrophic nitrifying bacteria as discussed by Healy et al. (2007) and Davidson et al. (2008), respectively. However, these reported studies were done on the wastewater matrix where biofilm growth rates are supposed to be high and form quickly too. In the drinking water matrix, the growth rate of such nitrifiers is not very high and hence NH_4-N removal depends a lot on the

physical properties of the adsorbent (here sand). Not surprisingly, the level of NH_4-N analyzed after the disinfection in either case (filter 1 or filter 2) showed no trace, due to a possible reaction of ammonia with hypochlorite ion (present in bleach) forming chloramine vapor. These chloramine vapors are strong irritants with the potential for tissue damage and are associated with quick resolution of symptoms for various respiratory diseases. The filtration unit in DWTP remains open to accessibility zone for the plant operators and may pose danger if they inhale during a long working hour shift. Hence, FM1 can be useful in reducing the NH_4-N level in surface water before it enters the disinfection units to deliver a safe working environment in the DWTP for the plant operators.

3.3.4 Iron, copper removal

The initial concentration of Fe^{2+} and Cu^{2+} present in the raw water was 10 mg/L and 20 mg/L (spiked according to their background concentration). Surprisingly, there was not much decrease in concentration that was observed for either of the metal ions after pre-oxidation (Table 2). For Fe^{2+}, coagulation removed a major portion by decreasing its concentration from > 8 mg/L to less than 5 mg/L. After sedimentation, some Fe^{2+} ions might have settled along with the suspended solids that formed flocs after coagulation (4.7 ± 0.55 mg/L to 3.1 ± 0.5 mg/L). After filtration from filter module 1, the concentration decreased further to < 1 mg/L while the filtrate of filter module 2 showed 2.3 ± 0.4 mg/L. Hence, the final Fe^{2+} concentration remained higher than the Canadian guidelines value (< 0.3 mg/L) for both cases. However, it is to be noted that the initial concentration of Fe^{2+} was more than the normal concentration found in the source water (1-5 mg/L). On the other hand, copper (Cu^{2+}) showed a distinct removal by filter module 1 as the residual Cu^{2+} concentration after sedimentation (12 mg/L) decreased to 2.6 ± 1.1 mg/L as compared to filter module 2 (6.6 ± 0.6 mg/L). High removal of both metal ions highlighted the

versatility of the GS1 media filter for the household purpose, especially for groundwater sources. As the treatment was analyzed each day for the iron and copper ions, the initial few days showed a non-detectable concentration after disinfection. However, after a few days, the precipitate was seen building at the bottom of the disinfection bottle, suggesting a possible residual metal ions build-up after reacting with the hypochlorite ions.

4. Impact of filter module 1 (½ GS1 filter + ½ Sand filter) in the treatment chain

Figure 5 shows the heat map of different WQPs analyzed for the treatment chain comprising filter module 1 (FM1) and filter module 2 (FM2). The common part in the heat map for both treatment chains were the results obtained for raw water tank, pre-oxidation tank, flocculation/coagulation and sedimentation tank. The green zone, light green zone, yellow zone, orange zone and red zone indicated a high, mid-high, average, low and poor removal of WQPs based on their guideline values for each treatment unit (designated as 1-6 on the y-axis of the heat mapping). These guideline values are mentioned in the caption of Figure 5. The right-hand side and left-hand side heat maps for a WQP represents the analysis of results for the treatment chain containing FM1 and FM2, respectively (thus color depiction for treatment unit 1-4 remains the same as discussed above).

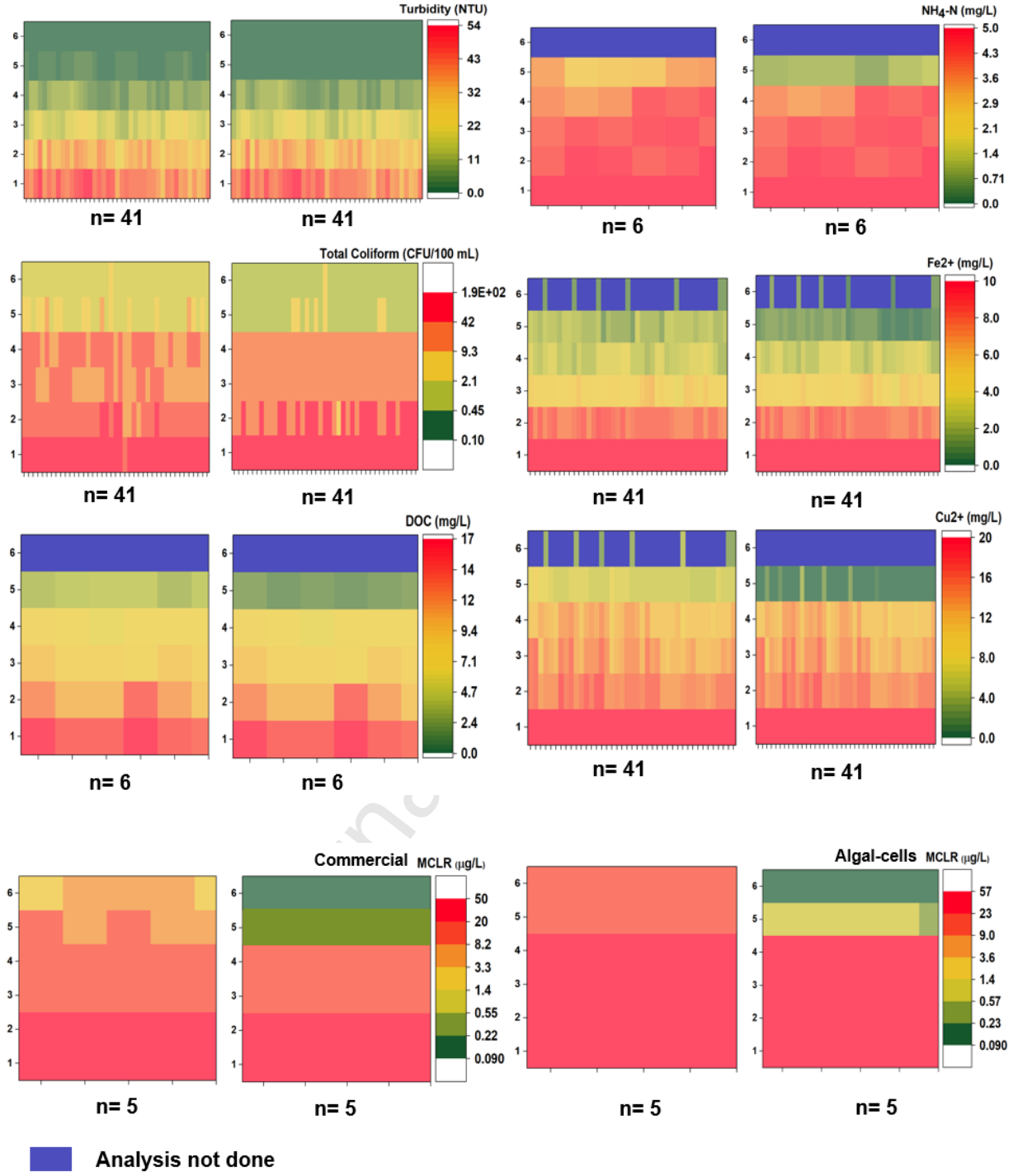

Figure 5: Heat map of different treatment units: 1) Raw water; 2) Pre-oxidation; 3) Coagulation/Flocculation; 4) Sedimentation; 5) Filter module 1 and 2 (left/right) and 6) Disinfection (these numbers are indicated on the y-axis of each heat map). Guideline values for turbidity <1 NTU, total coliform = NIL, ammonia-N is 0.121 mg/L, Fe^{2+} and Cu^{2+}: 0.3 mg/L and < 1 mg/L, respectively; MC-LR: < 1 µg/L; DOC: NIL (typically). The blue region depicts no sample done for that day. (Readers are advised to refer the online version of the article to see the color mapping)

The importance of FM1 for the removal of particular water pollutants can be observed via a heat map when compared with FM2 (control). For turbidity and total coliform removal, a greener zone in the heat map can be observed after the sedimentation unit for FM1 than FM2. However, the main contrast between treatment step 4 and step 5 (or sedimentation effluent and filter effluent) was observed for the DOC and ammonia-N parameter for FM1 treatment chain heat map as compared to the FM2 treatment chain heat map. Filtered effluent from FM1 showed safer and cleaner water quality (greener mapping) for over 41 days of the experiment, ensuring the applicability of FM1 for a longer period. Also, iron and copper showed a contrast heat mapping where FM2 treatment showed yellow to feeble green color as compared to the FM1 treatment where heat map showed green to a dark green color zone.

Heat map for two sources of MC-LR was also plotted to get a fair idea of the public safety in terms of a cleaner looking but a possible toxic-laden potable water. The heat map for the treatment chain comprising FM1 showed remarkable contrast to the FM2 treatment for both sources of MC-LR, where latter remained orange even after the disinfection treatment as compared to former which showed a green heat map. Among the two different sources of MC-LR tested, algal cells-derived MC-LR was found more difficult to get removed as compared to the commercial MC-LR until the sedimentation unit, which remained common for FM2 (as discussed above). It is interesting to observe the contrast in MC-LR removal for these two sources during pre-oxidation (potassium permanganate) step. There could be few theories related to the persistent nature of algal cells-based MC-LR as compared to commercial MC-LR during pre-oxidation. It should be noted that commercial MC-LR was prepared in methanol (2 ml methanol in 150 µg MC-LR vial) and then diluted appropriately using lake water (1.32 ml in 2 liters of lake water). On the other hand, algal cell-based MC-LR extract (40 ml) that consisted of

BG-11 media was diluted using 1960 ml lake water to prepare the MC-LR spiked raw water (as mentioned in section 2.6). Hence, there is a sign of lesser organic compounds present in the case of raw water prepared with commercial MC-LR. Thus, a difference in the type of matrix and its associated volume (< 0.1% for commercial MC-LR and 2% in case of algal cells-based MC-LR could be one of the reasons for a weak oxidation behaviour of permanganate ions in oxidizing MC-LR molecule. The second theory could be weak oxidation of MC-LR due to the presence of persistent by-products (proteins, hydrocarbons or lipids) associated with algal cell extract (present in BG-11 media) that was diluted at a greater strength (2%) as compared to the commercial MC-LR raw water preparation (<0.1%).

An impact factor was calculated considering the average score obtained for each WQP for both the filter modules. Table 3 tabulates the color (characteristic) obtained by averaging the color mapping of each sampling points (n=41 or 6 or 5 as shown in the heat map: Figure 5 for different WQP) with their average score calculated based on proximity achieved to the guideline value (calculation not shown here). An impact ratio was calculated for both the filter modules by Equation 1.

Total impact score for a filter module = $\sum_{i=1}^{i=n}(\text{score for WQPi})$

Impact ratio = (Total impact score for a filter module)/(n x 100) (1)

Where, n is the total number of water quality parameters analyzed = 8 (here) and i is the i^{th} WQP.

An ideal filter condition would have shown an impact ratio of 1.0. Overall, the average impact ratio of > 0.9 was observed for FM1 as compared to < 0.6 for FM2. This shows the impact of FM1 that consists of ½ GS1 filter. This further highlighted a poor adsorption property of sand

especially for the MC-LR water pollutant justifying the need for graphitized sand filter module in the drinking water treatment system or the household purpose.

Table 3: Average map color of the water quality parameter (WQPs) for filter module 1 and filter module 2

Water Quality Parameter (WQPs)	**Average color mapping**		**Average score FM1**	**Average score FM2**
	FM1	FM2	FM1	FM2
NH_4-N			75	35
Cu^{2+}			90	70
Fe^{2+}			92	75
Total coliform			90	90
Turbidity			90	75
DOC			90	80
Commercial MC-LR			100	30
Algal MC-LR			95	20
Total impact score			722	475
Impact ratio			0.91	0.59

DOC: Dissolved organic carbon; MC-LR: Microcystin-LR; FM1: Filter module 1 and FM2: Filter module 2
WQPs: Water Quality Parameters (Readers are advised to refer the online version of the article to see the color mapping)

Based on the average impact score for FM1 and FM2, FM1 showed an impact ratio of 0.91 against 0.59 for FM2. Lower ammonia-N, Cu^{2+}/Fe^{2+} and MC-LR removal from FM2 are mainly responsible for its lower impact ratio. However, it must be noted that though FM1 showed a very close impact ratio to 1 (ideal filter), it only shows its potential when tested using the parameters listed in Table 3. The current work did not mention the testing of other important WQPs (for either filter module) such as nitrate, nitrite, chlorine, amine compounds, fluoride, calcium and manganese ions. Hence, the impact ratio is very likely to further decrease if various other WQPs are added during quality testing.

5. Application feasibility of the filter module at the household level

This section discusses an overview of the techno-economic feasibility of the filter modules when used at the household scale. Instead of assessing two half filters (one module), the techno-economic study was done standalone-wise for sand and GS1 filter, according to the household filter version 10.0 as suggested by the Center for Affordable Water and Sanitation Technology (CAWST). Figure 6 shows the model of the household filter with dimensions and other details. Table 3 enlists all the materials and cost parameters estimated to produce filter material for both sand and graphitized sand filter. The cost calculation suggested that at large scale material production (material for 2200 sand filter units and 2900 GS1 filter units), one unit of GS1 filter cost was 65 CAD as compared to 46 CAD for the sand filter (excluding the indirect cost multipliers as shown in Table 3). Though the manufacturing unit cost of GS1 filter is 19 CAD more expensive than a sand filter, the inclusion of technical parameters makes it significantly economical (discussed next). All the necessary details and calculations are presented in Table 3. After including indirect cost multipliers according to the parameters listed in USEPA Point-of-Use (POU) and Point-of-Entry (POE) model cost evaluation document, the cost of GS1 filter and the sand filter comes out to be 87 CAD and 62 CAD, respectively (refer Table 3 and https://www.epa.gov).

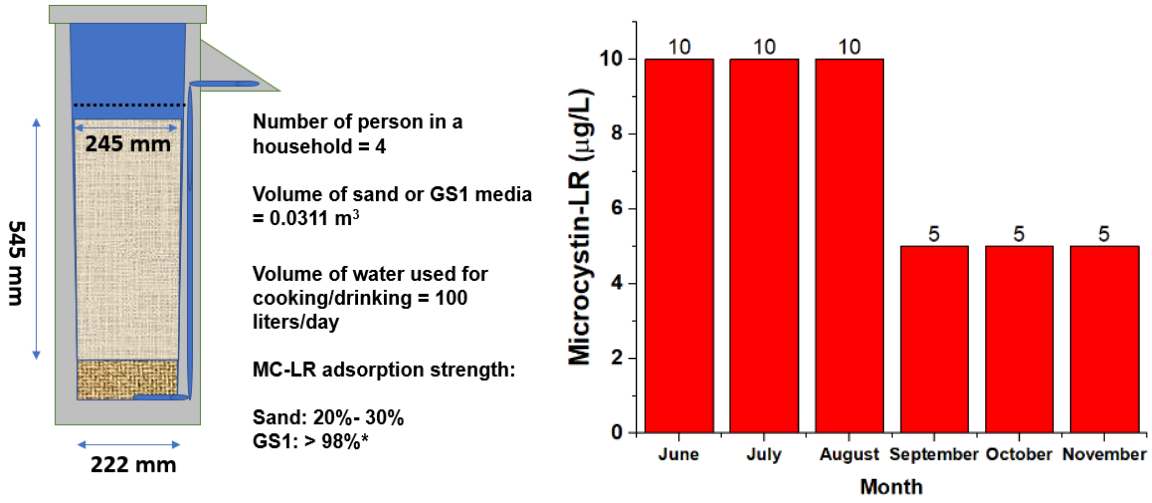

Figure 6: A) Schematic of biosand filter according to the guidelines of Center for Affordable Water and Sanitation Technology (CAWST) and B) Bar chart of the seasonal outbreak of MC-LR (with expected concentration) for 6 months with their expected concentration present in the source water

The technical performance of the filter was mainly judged based on the ability of the adsorbent material to remove MC-LR. From the results obtained in the current study and our earlier study using sand media (Kumar et al. 2020b), the average removal percent of MC-LR at an initial concentration of 50 µg/L stands at 20%-30% (no bioaugmentation case) and >98% for sand and graphitized sand material, respectively. For calculation, the following assumptions were made:

1) An average household comprises 4 people where 100 liters of water is utilized for cooking and drinking purpose.

2) From June to August (peak cyanobloom season) and September to November, the concentration of MC-LR in source water is assumed to be 10 µg/L and 5 µg/L, respectively (as shown in Figure 6).

The gross cost of a filter included the labour cost that may incur during operation and maintenance, monitoring, billings and flyers. Overall, the gross cost estimated for GS1 and sand filter was 232 CAD and 207 CAD, respectively. Based on the adsorbent efficiency and saturation

capacity (obtained from our previous study: Kumar et al. 2020b), the calculation showed (Table 3) that sand filter needed a change (based on the MC-LR breakthrough) in the adsorbent media after every 12 days as compared to after every 528 days for the graphitized sand filter (for calculation refer Table 3)**.** This means that every year, around 160 CAD is required for GS1-based household filters as compared to around 6210 CAD (equivalent) for the sand-based filter. According to the Unit Prices for POU Adsorptive Media NSF53 Equipment as mentioned in the USEPA Point-of-Use (POU) and Point-of-Entry (POE) model cost evaluation document, cost of 1 filter for household ranging 501-1000, should fall around $170 (equivalent to 231 CAD according to currency conversion rate as of 12 July, 2020). In the listed calculation (Table 3), the above price is very close to the gross price of one filter unit (232 CAD for GS-based filter and 207 for sand-based filter)

It must also be noted here that the MC-LR adsorbent capacity of a sand filter is 20%-30% and hence the calculated estimates are based on an equivalent basis, unlike GS-based filter which ensures >98% MC-LR removal each time it filters raw water.

Table 3: Techno-economic parameters and assessment of both adsorbent filters (household-level according to Center for Affordable Water and Sanitation Technology (CAWST)

Properties/items of cost	**Sand**	**GS1**
Economic performance parameters		
Density (Bulk) [gm/cc]	1.36	1.05
Density (Solid) [gm/cc]	2.68	2.16
Filter material volume (m3)	0.0311	0.0311
Material required per filter (kg)	42.3	32.7
a) Cost of raw sand (@ 0.548 CAD/kg)	23.18	17.92
Cost of sand per batch	512.9	512.9
b) Coating solution	NA	NIL
c) Other costs such as fittings, concrete mix, etc.	100	100
Processing time (operation)	1-2 hour	6 hours

Labour cost (100 CAD/hour)	200-400	1200
Number of technicians per batch of muffle/washing operation	2	2
Cost of muffle furnace (capital cost in CAD)	9800	9800
Power of muffle furnace	70 kW	70 kW
Electricity cost (0.1 CAD/kWh)	0	42
Number of filters per batch	22	29
Cost of 1 batch operation (including instrument cost) in CAD	10,713	11,555
Cost of 100 batches of operation in CAD	1,01,093	1,85,293
Cost of 1 filter (excluding indirect cost multipliers)	46	65
Indirect cost multipliers: a) Permitting (3% of IEC) b) Pilot testing (3% of IEC) c) Legal (3% of IEC) d) Engineering (15% of IEC) e) Contingency (10% of IEC)	3032 3032 3032 15160 10109	5558 5558 5558 27793 18529
Total Cost of 1 filter	62	87
Labor costs for device installation in the POU/POE model (1 hour)**	45	45
Monitoring cost during maintenance and shipping of samples (if needed) once a year***	50	50
Disposal cost	NIL	NIL
Cost of flyers and billing mailers***	50	50
Gross Cost of 1 filter in CAD	207	232

Technical performance parameters		
MC-LR adsorption performance	20%-30%	> 98%
Volume to be treated per day (in liters)	100	100

MC-LR adsorption capacity (µg/g)	0.11	5.99
MC-LR (June-August) cumulative adsorption (µg)	90,000	90,000
MC-LR (September-November) cumulative adsorption (µg)	45,000	45,000
Total target in 6 months (µg)	1,35,000	1,35,000
Adsorption capacity for 1 filter (µg)	4,522	1,95,772
Number of filter change needed per year (if MC-LR is active only for 6 months)	30	0.69
Frequency of filter change (days)	12.16	528
Annual service cost (based on providing MC-LR free water and frequency change#	= (30 x 207 CAD) = 6210 CAD	= (232 x 0.69) = 160 CAD

It is calculated on an equivalent basis as GS-based filter assured >98% MC-LR removal as compared to sand-based filter which achieves just 20%-30% MC-LR adsorption at any given time. Also, assuming MC-LR is present in drinking water for six months (active period); CAD: Canadian Dollar; **: Based on "Cost evaluation of point-of-use and point-of-entry treatment units for small systems: cost estimating tool and users guide (CEPOU)" section 2.5.2; ***: assumption value is taken and referred the cost structure from CEPOU.

6. Conclusion

A laboratory-made micro-model drinking water treatment plant (DWTP) set-up (named: SAP-1©) was evaluated for the removal of various water quality parameters (WQPs) including micropollutant: Microcystin-LR (MC-LR) using two filter modules in the same chain individually. Filter module 1 comprised of the graphitized sand filter as a half filter along with sand filter as the other half whereas two half sand filters together constituted filter module 2. FM1 performed well for most of the WQPs where a mean difference of 20%- 40% (in removal) was observed in the final treated value as compared to FM2. In brief, metal pollutants in the form of copper and iron, dissolved organic carbon, ammonia-N, turbidity, and total coliform were almost completely removed by FM1 to follow the norms of Canadian drinking water guidelines. MC-LR derived from the algal biomass showed more resistance to degradation as compared to the commercial one until sedimentation. However, the use of FM1 ensured complete removal while FM2 showed more than 8 µg/L and 20 µg/L of residual MC-LR in the filtered water

(initial concentration: 50 μg/L). Graphitized sand filter module showed 40%-50% more PP1A activity than a sand filter module that ensured a toxic-free MC-LR filtrate and hence fit for the public consumption. The standalone graphitized sand filter can be practiced commercially to offer a low-cost solution (160 CAD/year) as compared to a conventional sand filter (>6000 CAD/year) for a household purpose for effective removal of most WQPs during the seasonal or year-round outbreak of MC-LR in surface water if used directly as a source for drinking water.

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Conflict: None

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Credit Author Statement

Pratik Kumar: Conceptualization, Methodology, Data curation, Formal analysis Investigation, Writing - original draft. **Maximiliano Cledon:** Review & editing, Visualization. **Satinder Kaur Brar:** Review, Project administration; Resources Funding acquisition.

Declaration of competting interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract

Highlights:

- Graphitized sand filter showed 20%-50% higher efficiency in removal of water pollutants than a sand filter.
- Graphitized sand (GS1) household filter cost 160 CAD as compared to >6000 CAD for sand filter
- MC-LR was 100% removed by GS filter and showed 50% more PP1A activity than a sand filter
- Water quality score for GS1 and sand filter was 722 and 475, respectively (out of 800)