Improving energy efficiency of electrochemical blackwater disinfection through sequential reduction of suspended solids and chemical oxygen demand [version 2; peer review: 2 approved]

Brian T. Hawkins\textsuperscript{1,2}, Tate W. Rogers\textsuperscript{3}, Christopher J. Davey\textsuperscript{4}, Mikayla H. Stoner\textsuperscript{1,2}, Ewan J. McAdam\textsuperscript{4}, Brian R. Stoner\textsuperscript{1,2}

\textsuperscript{1}Center for WaSH-AID, Duke University, Durham, NC, 27701, USA  
\textsuperscript{2}Department of Electrical and Computer Engineering, Duke University, Durham, NC, 27701, USA  
\textsuperscript{3}Triangle Environmental Health Initiative, Durham, NC, 27701, USA  
\textsuperscript{4}Cranfield Water Sciences Institute, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

\textbf{Abstract}
Onsite reuse of blackwater requires removal of considerable amounts of suspended solids and organic material in addition to inactivation of pathogens. Previously, we showed that electrochemical treatment could be used for effective pathogen inactivation in blackwater, but was inadequate to remove solids and organics to emerging industry standards. Further, we found that as solids and organics accumulate with repeated recycling, electrochemical treatment becomes less energetically sustainable. Here, we describe a pilot study in which concentrated blackwater is pretreated with ultrafiltration and granular activated carbon prior to electrochemical disinfection, and show that this combination of treatments removes 75-99\% of chemical oxygen demand, 92-100\% of total suspended solids, and improves the energy efficiency of electrochemical blackwater treatment by an order of magnitude.

\textbf{Keywords}
Sustainability, water reuse, electrochemical disinfection, ultrafiltration, activated carbon, blackwater
Corresponding author: Brian T. Hawkins (brian.hawkins@duke.edu)

Author roles: Hawkins BT: Conceptualization, Formal Analysis, Funding Acquisition, Investigation, Methodology, Project Administration, Visualization, Writing – Original Draft Preparation; Rogers TW: Conceptualization, Methodology, Resources, Writing – Review & Editing; Davey CJ: Resources, Writing – Review & Editing; Stoner MH: Investigation, Writing – Review & Editing; McAdam EJ: Conceptualization, Resources, Writing – Review & Editing; Stoner BR: Conceptualization, Funding Acquisition, Writing – Review & Editing

Competing interests: No competing interests were disclosed.

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Introduction

Electrochemical disinfection is a promising approach to sustainable decentralized waste water treatment because it enables oxidative inactivation of pathogens without requiring onsite storage of disinfecting chemicals (e.g., sodium hypochlorite or chlorine gas). In systems that utilize recycled blackwater for flushing, these processes become more energy intensive over time as solids accumulate in the process liquid. Understanding how the constituents of blackwater that accumulate in such systems contribute to the decreased efficiency of electrochemical disinfection is key to developing remediation strategies that will enable practical implementation and long service lifetimes.

Previously, we investigated the effects on electrochemical disinfection energy efficiency of removing total suspended solids (TSS) with improved settling tank design and removing chemical oxygen demand (COD) with granular activated carbon (GAC) and found that only the latter resulted in a significant improvement. This implied that soluble COD was the principle cause of diminishing efficiency with repeated recycling of blackwater. However, because we had not completely removed TSS in any of these studies, we could not conclude definitively that suspended solids did not contribute. We also found that the same GAC media could remove a substantial fraction of blackwater COD in multiple treatment batches—suggesting that the filter medium was not fully saturated in these experiments—but that within each batch up to half of COD could not be readily removed by GAC. Thus, we hypothesized that this poorly adsorbing fraction of COD was associated with suspended particulate matter not removed by settling or GAC, and further, that successful removal of this fraction from blackwater would improve the energy efficiency of subsequent electrochemical disinfection. We tested this hypothesis in a pilot study in which blackwater was treated by cross-flow ultrafiltration followed by a GAC packed bed filter, and assessed the effect of these combined pre-treatments on the energy required for subsequent electrochemical disinfection.

Methods

Blackwater was collected from a prototype blackwater recycling toilet system previously described. Procedures for the collection of human urine and feces used to generate blackwater were reviewed and approved by Duke University’s Institutional Review Board. Characteristics of the untreated blackwater used in this study are shown in Table 1.

Ultrafiltration was carried out in 8–12 L batches by passing blackwater through an ultra-high molecular weight polyethylene tubular membrane with a nominal pore size of 0.02 µm and a total active surface area of 0.07 m² (Porex, Norcross, GA, USA) with a centrifugal pump (Lowara, Montecchio Maggiore, Italy) run in a recirculation configuration. In these experiments, flow was maintained between 28 and 30 L min⁻¹ for a cross flow velocity in the retentate channel of 3.7 – 3.9 m s⁻¹. Transmembrane pressures were monitored by pressure transducers (Omega PX039-015G5V, Omega, Norwalk, CT) on either side of the membrane connected to an Omega OM-DAQ-USB-2400 data logger, and during ultrafiltration typically ranged between 2 and 2.5 bar. Transmembrane flux was monitored by placing the permeate collecting vessel on a balance connected to a computer and using ADAM DU software to log changes in mass, and during ultrafiltration typically ranged between 80 and 120 kg m⁻² h⁻¹ (Figure S1).

Ultrafiltered blackwater was passed through a packed bed column filter with Aquacarb® 830, an 8 × 30 mesh-sized GAC derived from bituminous coal (Evoqua, Pittsburgh, PA), as the medium. The filter consisted of 1.8 kg GAC in a PVC pipe (9.4 cm inner diameter) with a media length of 58 cm, a media volume of ~4 L, and an interstitial volume of ~1 L. Liquid was pumped through at a rate of ~1 L min⁻¹ in a recirculation configuration for up to 18 h. In a subset of experiments, COD was monitored during the first ~2 h of GAC treatment to evaluate the COD removal kinetics of GAC with ultrafiltered blackwater in comparison to untreated blackwater (Figure S2).

Electrochemical disinfection was performed as previously described in an 8-L HDPE tank with a commercially available electrochemical cell (Hayward Salt&Swim 3C) run at 24 VDC. This process effects disinfection by oxidizing chloride (primarily from urine) into chlorine. Measurements of water quality parameters were performed as previously described in detail. Bacterial inactivation was assessed with a 3-well most probable number (MPN) method using lysogeny broth (LB) for dilution and culture as previously described in detail. Disinfection was defined...
as reduction of MPN to < 5 / ml; energy required to achieve this level of disinfection was calculated as previously described and shown in Figure S3.

Statistical analyses and visualizations were performed using GraphPad Prism v7.04.

Results and discussion
Results are presented in Figure 1. Ultrafiltration significantly reduced blackwater COD by an average of 55% (range 32–74%) and TSS by an average of 97% (range 92–100%). Subsequent treatment with GAC was associated with further reduction of COD to near or below the ISO 30500 category B standard (150 mg/L) for an average total COD reduction of 87% (range 75–99%). These reductions in COD and TSS were associated with a reduced energy demand for the electrochemical process to achieve the desired disinfection threshold to an average of 8.5 kJ/L, which represents an order of magnitude improvement compared with the same process using untreated blackwater (70 kJ/L).

For the purposes of this study we defined disinfection as MPN < 5 / ml; as we have found little to no bacterial regrowth in blackwater treated beyond this threshold. Since many species of bacteria grow in suspension in LB, including coliforms, this method and threshold serve as a conservative estimate of treatment required to inactivate pathogenic bacteria in blackwater. However, an important limitation of this study is that we did not assess the ability of this process for inactivation of viruses, protozoa, or helminth eggs. Future studies on this process will address specific pathogen removal, in particular the surrogates indicated by the recently published ISO 30500 standard.

Treating blackwater first with ultrafiltration, then with activated carbon, followed by electrochemical treatment, has specific advantages. The removal of suspended solids by ultrafiltration appears to allow for faster adsorption of soluble species by subsequent GAC treatment, which could make GAC treatment in a single-pass configuration practical and thus eliminate the need for a recirculating pump (Supplemental Data, Figure S2). Further, the removal of suspended solids minimizes the tendency

Figure 1. Pilot study combining ultrafiltration (UF) and granular activated carbon (GAC). A and B: improvements in chemical oxygen demand (COD) and total suspended solids (TSS), respectively, with UF followed by GAC. Data are n = 5 batches, measurements taken sequentially in each batch. Dotted lines indicate ISO 30500 category B standards (150 mg/L COD and 30 mg/L TSS). Significance determined by repeated measures one-way ANOVA with a Tukey’s multiple comparisons test. * = adjusted p < 0.05 vs. untreated, ** = adjusted p < 0.01 vs. untreated. + = adjusted p < 0.05 vs. UF, ++ = adjusted p < 0.01 vs. UF. C: Comparison of energy required to achieve disinfection (MPN < 5/ml) of blackwater treated by UF and GAC prior to electrochemical disinfection (n=5) to untreated blackwater (n=18). Untreated data are from a previous study. Significance determined by two-tailed t-test, **** = p < 0.0001. A–C: lines indicate median, boxes 25th and 75th percentiles, error bars maximum and minimum values. D: Samples of untreated, UF treated, and UF + GAC treated blackwater (left to right).
of the GAC packed bed filter to clog, thus obviating the need for frequent backwashing.

Cross-flow ultrafiltration requires considerable energy input to the pump to achieve the necessary cross-flow velocity needed for practical membrane productivity. The test rig used for these studies uses a ¾ horsepower-rated pump, and runs at ~850 W when processing blackwater. Based on the runtimes of each trial (Figure S1) we estimate the energy cost for ultrafiltration in these studies to be 391 ± 60 kJ/L, which is significantly more than the 62.5 kJ/L gain in energy efficiency realized in the electrochemical process (Figure 1C). It is important to point out, however, that we have not yet optimized this process for the treatment of blackwater, and that an in-depth study of optimal running parameters (cross flow velocity, transmembrane pressure, and membrane surface area) is expected to yield a more efficient process.

Furthermore, the reductions in TSS and COD with the combination of ultrafiltration and GAC far exceed anything we have achieved with electrochemical oxidation alone. We’ve run the electrochemical process used here on untreated blackwater for considerably longer than is required to achieve disinfection, and found that energy expenditures greater than what the unoptimized ultrafiltration process requires (471 – 575 kJ/L) only resulted in 32–38% reduction in COD and no significant reduction in TSS. Thus, while ultrafiltration adds complexity to the system and increases the overall energy demand compared with electrochemical oxidation alone, this is likely an unavoidable tradeoff in order to treat blackwater to ISO 30500 effluent standards.

This pretreatment regime allows for shorter runtimes on the electrochemical process, which will prolong the service lifetime of the electrodes. Similarly, disinfection of pretreated blackwater is achieved with much lower free chlorine concentration-time product (CT) (< 50 mg min/L) compared to untreated blackwater (which can require CT in excess of 2000 mg min/L to be disinfected). This reduces the duration of time system components (plumbing, tanks) will need to be in contact with the highly oxidative chemistry of the process liquid and thus increase their service lifetime.

Conclusions
Further optimization of the component processes to minimize energy and capital costs and a more thorough assessment of component life cycle and efficacy in specific pathogen removal are necessary to reduce this approach to practice. Although these results are preliminary, we believe they serve as a proof of concept for a practical approach to onsite blackwater treatment that will meet emerging industry standards.

Data availability
Raw datasets are available on OSF, project “Improving energy efficiency of electrochemical blackwater disinfection through sequential reduction of suspended solids and chemical oxygen demand”, https://doi.org/10.17605/OSF.IO/GRMJ6.

Data are available under the terms of the Creative Commons Zero “No rights reserved” data waiver (CC0 1.0 Public domain dedication).

Grant information
This study is supported by a Bill & Melinda Gates Foundation [OPP1164126].

The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Supplementary material
Figure S1: Ultrafiltration runs. Shown are plots of the transmembrane flux (in red) and transmembrane pressure (TMP, in blue) for each of the five ultrafiltration runs in this report.

Click here to access the data.

Figure S2: Effect of ultrafiltration of COD removal by GAC. Shown are plots of COD in one experiment with untreated blackwater and two with ultrafiltered blackwater. Blackwater was treated in 8-L batches by continuous recirculation at ~1 L min⁻¹.

Click here to access the data.

Figure S3: Disinfection curves and energy calculations. Shown are plots of each electrochemical disinfection run following ultrafiltration and GAC treatment. Black dotted line indicates the disinfection threshold (MPN < 5/ml), red dotted line indicates the disinfection energy (Eₜ) interpolated from where the plot crosses the disinfection threshold.

Click here to access the data.
References


Srikanth Mutnuri

Applied Environmental Biotechnology Laboratory, Department of Biological Sciences, Birla Institute of Technology and Science, Goa, India

The work focusses on minimizing the running cost of the electrochemical system by incorporating ultrafiltration and granular activated carbon. The results also show that there is reduced energy demand for running electrochemical system.

However, it will be interesting to show the total recurring expenditure. Although there is less energy demand, it will be interesting to see the running cost for this arrangements as there will be requirement / replacement of membrane and granular activated carbon on a longer run.

It would have been better if the authors have done repeated cycles of treatment so as to ascertain the life of the membrane and GAC.

This seems to be a simple adsorption way of treatment! What happens to the solids that is accumulated due to membrane and GAC?

How disinfection is proved in these experiments is not clear? Is there any special coating on the electrodes? If yes, what is it and what will be generated (hypochlorite etc) during treatment and what is the life of the coating?

Why did the authors chose Membrane and GAC over other passive treatment techniques available?

Can the membrane and GAC will be able to trap Helminthes eggs?

Is the work clearly and accurately presented and does it cite the current literature? Yes

Is the study design appropriate and is the work technically sound?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?  
Yes

If applicable, is the statistical analysis and its interpretation appropriate?  
Yes

Are all the source data underlying the results available to ensure full reproducibility?  
Yes

Are the conclusions drawn adequately supported by the results?  
Partly

**Competing Interests:** No competing interests were disclosed.

**Reviewer Expertise:** Environmental biotechnology

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

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**Author Response 14 Jan 2019**

**Brian Hawkins**, Duke University, Durham, USA

We thank Dr. Mutnuri for the review, and share his desire to learn more about the running costs and life cycles of these components and processes! Point by point comments follow.

The work focusses on minimizing the running cost of the electrochemical system by incorporating ultrafiltration and granular activated carbon. The results also show that there is reduced energy demand for running electrochemical system.

However, it will be interesting to show the total recurring expenditure. Although there is less energy demand, it will be interesting to see the running cost for this arrangements as there will be requirement / replacement of membrane and granular activated carbon on a longer run.

**As noted in our reply to Dr. DeLong, we have greatly expanded the discussion of energy costs and the tradeoffs involved.**

It would have been better if the authors have done repeated cycles of treatment so as to ascertain the life of the membrane and GAC.

**Also as noted above, a rigorous analysis of component lifetime is underway in field tests.**

This seems to be a simple adsorption way of treatment! What happens to the solids that is
accumulated due to membrane and GAC?

In practice, GAC will need to be replaced or regenerated. Defining how frequently this needs to occur is one of the goals of the aforementioned field tests.

Ultrafiltration does result in a concentration of suspended solids over time in the feed tanks, which do need to be periodically cleaned out. There are several options for dealing with such a concentrated slurry, including anaerobic digestion or emptying into a containment unit that is periodically pumped out (pit, septic tank, etc.). In any case, the concentration of these solids reduces the burden of containing and transporting them significantly.

How disinfection is proved in these experiments is not clear? Is there any special coating on the electrodes? If yes, what is it and what will be generated (hypochlorite etc) during treatment and what is the life of the coating?

In V2 we’ve added to the Methods: “This process effects disinfection by oxidizing chloride (primarily from urine) into chlorine.”
And: “Bacterial inactivation was assessed with a 3-well most probable number (MPN) method using lysogeny broth (LB) for dilution and culture as previously described in detail 1-4. Disinfection was defined as reduction of MPN to < 5 / ml”

Why did the authors chose Membrane and GAC over other passive treatment techniques available?

We were (and are) primarily interested in minimizing COD in the fastest and least space-intensive ways practical, since we are working towards systems for application in urban settings.

Can the membrane and GAC will be able to trap Helminthes eggs?

We have every reason to expect helminth eggs to be size-excluded by the membrane filtration unit, but we will be confirming this in the near future pursuant to testing to the ISO standard.

**Competing Interests:** No competing interests were disclosed.
This work investigated the value of ultrafiltration (UF) and GAC treatment for removal of solids and dissolved organics for application in a novel toilet based on electrochemical treatment. Although this is only a technical note, I found details lacking that made it difficult to fully appreciate the value of the work. Additionally, the authors appeared to focus only on the energy involved in the electrochemical treatment with and without the UF and GAC. A more comprehensive assessment considering the life cycle costs and energy use associated with UF and GAC would be more useful. Also, the method used to assess disinfection is very basic and may fail to detect critical classes of pathogens.

Specific comments and suggestions:
1. Given that disinfection is a critical aspect of this work, I suggest the authors clearly explain the methods used in the text. What media was used and what is expected to grow on this media, for example? Why not run total and fecal coliform analyses? Additionally, I am concerned that this approach does not provide a full picture of disinfection efficacy. The methods used do not provide information regarding protozoa or viruses, both of which I expect to be of critical importance. I suggest the authors specifically acknowledge these limitations in the text to avoid any miscommunication. Further, I would suggest that future studies consider a much broader range of microbial pathogens. The authors might also give consideration to whether bacteria can become viable but not culturable (VNBC) upon electrochemical treatment.

2. What is the energy and material cost associated with UF and GAC? How long can the UF and GAC filters last before they need to be replaced with normal use? How would spent GAC be handled?

3. It would be nice to comment on the possibility of phosphorus recovery.

4. In Fig. S3, are all these data for after UF & GAC? Please clarify. It would be nice to see some comparisons with and without UF and GAC.

5. It would be helpful to more clearly explain how the electrochemical system works/will be operated such that oxidative plumbing and tanks will have less exposure to oxidative chemistry.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and is the work technically sound?
Partly

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Yes

Are all the source data underlying the results available to ensure full reproducibility? Yes

Are the conclusions drawn adequately supported by the results? Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Environmental engineering, biological treatment processes, applied microbiology, and molecular biology tools

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Author Response 14 Jan 2019

Brian Hawkins, Duke University, Durham, USA

We greatly appreciate the thoughtful and thorough review from Dr. De Long. Point by point responses follow.

This work investigated the value of ultrafiltration (UF) and GAC treatment for removal of solids and dissolved organics for application in a novel toilet based on electrochemical treatment. Although this is only a technical note, I found details lacking that made it difficult to fully appreciate the value of the work. Additionally, the authors appeared to focus only on the energy involved in the electrochemical treatment with and without the UF and GAC. A more comprehensive assessment considering the life cycle costs and energy use associated with UF and GAC would be more useful. Also, the method used to assess disinfection is very basic and may fail to detect critical classes of pathogens.

Specific comments and suggestions:

1. Given that disinfection is a critical aspect of this work, I suggest the authors clearly explain the methods used in the text. What media was used and what is expected to grow on this media, for example? Why not run total and fecal coliform analyses? Additionally, I am concerned that this approach does not provide a full picture of disinfection efficacy. The methods used do not provide information regarding protozoa or viruses, both of which I expect to be of critical importance. I suggest the authors specifically acknowledge these limitations in the text to avoid any miscommunication. Further, I would suggest that future studies consider a much broader range of microbial pathogens. The authors might also give consideration to whether bacteria can become viable but not culturable (VNBC) upon electrochemical treatment.

In V2, we have added some additional detail to the Methods. We have also added a paragraph to the Results (Now Results and Discussion) outlining our rationale for using the non-specific MPN method, and acknowledging the limitations that Dr. De
Long (correctly) points out. As now noted in V2, a follow up study is planned that will include testing of specific pathogens/surrogates per the ISO 30500 standard.

2. What is the energy and material cost associated with UF and GAC? How long can the UF and GAC filters last before they need to be replaced with normal use? How would spent GAC be handled?

In V2, we have added considerable discussion of the energy cost associated with UF. (The energy cost associated with GAC is trivial by comparison, particularly if GAC treatment is done in single pass which is our plan going forward.)

Assessment of component lifetime is underway. We have been field testing some GAC columns with blackwater for many months with promising results, which we hope to be publishing soon. Field tests with the specific goal of defining mean time to failure with both UF and GAC in blackwater treatment will be happening this year (2019).

Ultrafiltration has been applied at scale in wastewater treatment for over thirty years. An original estimate made for UF membrane life expectancy was around 7 years but the replacement frequency was lower than expected and as such longer asset lifetimes have been observed. One critical determining factor is in the extent of chemical cleaning mandated. Within this short term trial, the conversion factor, together with the trade-off between permeation rate (flux) and cross flow velocity were not optimised. These factors determine chemical cleaning frequency and the intensity of the conditions within which the membrane will be operated – both factors being a function of how hard the membrane is run (therefore limiting capital cost). Further examination of this relationship will be undertaken in future investigations to identify sustainable conditions incurring the least whole life cost, or least capital cost.

3. It would be nice to comment on the possibility of phosphorus recovery.

Evaluation of this process for phosphorus (and nitrogen) removal is underway, pursuant to testing to the ISO 30500 standard, and those data will be published in the aforementioned follow-up study.

4. In Fig. S3, are all these data for after UF & GAC? Please clarify. It would be nice to see some comparisons with and without UF and GAC.

Fig S3 is mainly meant to show how the energy of disinfection is calculated. The legend for this figure does indicate that the “...are plots of each electrochemical disinfection run following ultrafiltration and GAC treatment.”

We didn’t show the curves from control experiments in the supplemental figure because 1) the summary plot in Fig 1C serves the purpose of comparison, 2) there were 18 experiments in that data set, and 3) these data are already published. Further, we didn’t want to show a subset of those experiments on the XY plots in the supplemental figure because we didn’t want to give the impression that these were “matched” experiments; however, showing all of them on a single plot with more than
a few curves renders the figure unintelligible.

5. It would be helpful to more clearly explain how the electrochemical system works/will be operated such that oxidative plumbing and tanks will have less exposure to oxidative chemistry.

In V2 we've re-written the relevant section to emphasize that we are talking about the smaller concentration-time product required to achieve disinfection: “...disinfection of pretreated blackwater is achieved with much lower free chlorine concentration-time product (CT) (< 50 mg min / L) compared to untreated blackwater (which can require CT in excess of 2000 mg min / L to be disinfected) ¹. This reduces the duration of time system components (plumbing, tanks) will need to be in contact with the highly oxidative chemistry of the process liquid and thus increase their service lifetime.”

**Competing Interests:** No competing interests were disclosed.