

**BIOLOGICAL AND MEMBRANE TREATMENT APPLICATIONS
FOR THE REDUCTION OF SPECIFIC CONDUCTIVITY AND
TOTAL DISSOLVED SOLIDS IN COAL MINE WATERS**

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ABSTRACT (ACADEMIC)

Specific conductivity (SC) and total dissolved solids (TDS) are increasingly being used as a parameter used to judge the aquatic health of streams that are impacted by coal mining operations in the Appalachian region of the United States. Due to this, government environmental regulatory bodies have been considering issuing a regulation on SC for all mining operation outfalls. Sulfate typically has the greatest dissolved ion presence in coal mine waters. In literature examining the treatment of mine waters, SC and TDS analysis is typically not reported. The technologies examined in this study were nanofiltration membrane technology and biological sulfate reducing bioreactors.

In the nanofiltration study, three different nanofiltration membranes were evaluated for SC reduction: NF270, DK, and NFX. The DK and NFX nanofilters were able to reduce SC levels by an average of 84 percent for both mine waters tested and were able to reach SC levels below the proposed limit of 500 $\mu\text{S}/\text{cm}$. The SC levels achieved by the NF270 nanofilters were observed to have much higher variability. The inclusion of microfiltration and simulated-sand filtration were also introduced as a pre-treatment stage in order to determine whether or not nanofiltration performance would improve in terms of SC reduction.

In the biological sulfate reducing bioreactor study, multiple bioreactors were established to identify the optimal organic mixture to foster both SC and sulfate reduction. Sulfate reduction began to occur approximately 20 days after the establishment of each bioreactor. SC levels were greater than 13,000 $\mu\text{S}/\text{cm}$ in each of the bioreactors sampled by the fortieth day of sampling. The probable cause of the increase SC was identified to be the manure/compost used in the study. Future testing should incorporate more sampling in the early phases of experimentation in order to ensure the ability to monitor changes in water quality.

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ABSTRACT (PUBLIC)

Treatment technologies used to treat coal mine waters have traditionally focused on mitigating pH, dissolved oxygen, ferric iron, and aluminum levels. Specific conductivity (SC) and total dissolved solids (TDS) have been identified in recent years to be deterrents of aquatic health in coal mine waters. Sulfate in particular has been found to be a contributor of SC and TDS that can cause a deterioration in aquatic health. There is an apparent gap of knowledge as it pertains to the reporting of the reduction of SC and TDS in coal mine waters.

The objective of this study was to evaluate the utilization of nanofiltration membrane technology and biological sulfate reduction as methods for reducing SC and TDS in coal mine waters of southwestern Virginia. Three nanofiltration membranes with various characteristics were tested in order to determine whether they could meet literature recommended SC levels. Microfiltration and simulated sand filtration were incorporated as pretreatment steps in order to determine if these could stimulate further SC reduction. Major water quality characteristics were monitored after nanofiltration as well.

Multiple biological sulfate reduction reactors were designed in the second part of the study and allowed to treat coal mine waters for a 40-day period. Each reactor tested used varying mixtures in order to determine the optimal mixture for both sulfate and SC reduction. Reactors were sampled periodically for the monitoring of major water quality parameters.

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LIST OF ABBREVIATIONS

AMD	Acid Mine Drainage
BH	Barton Hollow
BSR	Biological Sulfate Reduction
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CWA	Clean Water Act
DOC	Dissolved Organic Carbon
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IC	Ion Chromatography
NPDES	National Pollutant Discharge Elimination System
OF	Office Fill
OSMRE	Office of Surface Mining Reclamation and Enforcement
RO	Reverse Osmosis
SC	Specific Conductivity/Conductance
SO ₄ ²⁻	Sulfate
SMCRA	Surface Mining Control and Reclamation Act
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
WWTP	Wastewater Treatment Plant

Chapter 1 – INTRODUCTION

Objectives

The objective of this study was to evaluate membrane technologies and biological sulfate reduction in their ability to reduce specific conductivity (SC) and total dissolved solids in coal mine waters emanating from valley-fill structures. Demand for investigation into SC and TDS reducing technologies has increased in recent years due to an uptick in literature identifying correlations between SC/TDS and aquatic health of streams that our impacted by mining operations. In particular, sulfate has a large presence in coal mine waters coming from valley-fill structures and has been identified as an environmental concern in large concentrations. Based on these environmental concerns, a proposed SC limit of 500 $\mu\text{S}/\text{cm}$ has been considered.

A critical review of the literature pertaining to the topics of this study is introduced first (*Chapter 2*).

The feasibility of using nanofiltration membranes to reduce SC and TDS is then evaluated (*Chapter 3*). The objectives of this chapter were as follows:

- Determine whether or not nanofiltration could meet SC limit of 500 $\mu\text{S}/\text{cm}$
- Identify the top performing nanofilters
- Identify the optimal pretreatment technology to go along with nanofiltration
- Determine which ions were removed significantly by nanofiltration

The feasibility of using biological sulfate reduction to treat mine waters of southwestern Virginia is then evaluated (*Chapter 4*). The objectives of this chapter were as follows:

- Determine whether or not biological sulfate reduction could meet SC limit of 500 $\mu\text{S}/\text{cm}$ and reduce sulfate levels
- Identify cause of changes in SC
- Determine optimal bioreactor mixture for treatment of coal mine waters of southwestern Virginia

Final conclusions for this body of work are then introduced in *Chapter 5*.

Chapter 2 – LITERATURE REVIEW

Review of Regulations

Coal mining operations in the United States are governed by the following legislation at the federal level: the Clean Water Act of 1972 (CWA) and the Surface Mining Control and Reclamation Act of 1977 (SMCRA). Each of these pieces of legislation govern different aspects of mining operations as it pertains to regulating the effluent produced from mining operations. The effluent produced by mining operations can vary in terms of water quality depending on the type of coal mining operation. In southwestern Virginia, valley fill structures are typically used to store excess overburden materials from surface mining; these valley fill structures have been found to produce impaired waters (Evans et al., 2014).

The CWA, passed in 1972, established the National Pollution Discharge Elimination System (NPDES) permitting system, which involves the regulation of point source effluent producers. State environmental agencies issuing the NPDES permits to mining operations set effluent limits based on the more conservative standard between established effluent limitations or guidelines (ELGs) or a predetermined water quality criteria (US EPA, 2008). The specific water quality parameters regulated by NPDES permits traditionally varies depending on the type of effluent produced by the mining operation. For both acidic and alkaline mine waters, the following parameters are regulated by the NPDES permit: pH, iron, and total suspended solids (TSS); for acidic waters, manganese is regulated additionally (US EPA, 2008).

SMCRA was critical in establishing the Office of Surface Mining Reclamation and Enforcement (OSMRE), which was created to regulate both active and abandoned mining operations. When obtaining a mining permit from OSMRE, mining operations are required to submit a hydrological study that examines the anticipated water quality consequences of the mining operation (Surface Mining Control and Reclamation Act of 1977). As it pertains to mining effluent, SMCRA set forth regulations in order to reduce the leaching of acid-forming materials into surface water and groundwater. A controversial provision within SMCRA allows mining operations to use topsoil alternatives as overburden materials when topsoil layers are less than 15 inches in thickness; studies have found these

topsoil alternatives are a major contributor of dissolved ions in mining impaired waters (Orndorff et al., 2010).

The addition of specific conductance (SC) as a regulated water quality parameter became a concern for coal mining operations after a US Environmental Protection Agency (EPA) news release identified a SC range of 300-500 $\mu\text{S}/\text{cm}$ as an ideal target in order to protect water quality. This release was supported by Cormier et al. (2011) that had recommended a SC benchmark of 300 $\mu\text{S}/\text{cm}$ based on the health of macroinvertebrate organisms in mine impaired waters. Ultimately no SC regulation was passed based on the news release after litigation, however the potential of a SC standard has made the mining industry begin to examine ways to reduce SC as a precaution.

Common Water Quality Characteristics

When evaluating mining-impaired waters, SC and total dissolved solids (TDS) are increasingly becoming the most important water quality characteristics to consider in regards to the level of impairment of receiving streams from valley fills. There are a variety of factors that can impact the severity of SC and TDS levels in the receiving streams based on the coal mining operation.

SC, also known as conductivity, is a measure of the electrical conductance of a water sample. Standard values of SC tend to vary depending on the source of the water sample. For reference, standard values of SC for freshwater and ocean water are 100 $\mu\text{S}/\text{cm}$ and 50,000 $\mu\text{S}/\text{cm}$, respectively (Sanders, 1998). TDS is a measure of all the dissolved ions found in a water sample. TDS can be calculated by combining the concentrations of all the cations and anions found in a water sample.

Both SC and TDS can be measured using a probe/meter, however most systems incorporate a preset ratio that calculates the TDS based on the measured SC value. SC and TDS can be related by a ratio that typically ranges from 0.5 to 1.0 (Oram, 2014). When evaluating water quality, quantifying TDS using a standardized method should be used in order to determine a SC/TDS ratio that is suitable to the water being sampled. Under Standard Methods (Rice et al., 2012), TDS is determined through a multi-stage process that involves the following steps: filter sample through a standard glass fiber filter; heat a predetermined amount of filtrate at 180°C for an hour; measure weight of remaining solids.

For mine waters, typically very little filtrate is needed to conduct a TDS test due to high concentrations of various ions.

As previously mentioned, water quality from coal mining operations can vary depending on the type of coal mining operation and local geology. Overburden materials used in valley fills will contribute varying levels of dissolved ions to receiving streams. Mine impaired waters are generally categorized based on its pH and dominant dissolved ion present in the water. Orndorff et al. (2010) identified the dominant ions in coal mine waters to be sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). For acid mine drainage (AMD), water samples tend to be acidic and have elevated levels of iron and aluminum to go along with the other dominant ions mentioned above. Due to elevated iron concentrations, AMD generally has an orange color. The ion with greatest concentration for both AMD waters and that characteristic of southwestern Virginia has been found to be SO_4^{2-} (Merovich et al., 2007).

In southwestern Virginia valley-fill coal mining operations, mine water effluent would not be considered AMD. Water samples collected from this region were categorized by having near-neutral pH, low iron and aluminum concentrations, and moderate levels of SC/TDS. Like AMD, sulfate is typically the ion with the highest concentration found in southwestern Virginia coal mine-impaired waters. Due to the absence of iron, the mine impaired waters of southwestern Virginia are generally low in turbidity and have very little color.

Environmental Impacts of High TDS

The effects of TDS and SC on surface water systems has been the focus of research in recent years. In regards to water quality, an increase in TDS and SC has been found to lead to the salinization of receiving bodies of water and potentially affect stream aesthetics. Despite the long-term salinization of receiving streams coming valley fills, a study has found that the receiving streams would eventually regress back to SC levels below 500 $\mu\text{S}/\text{cm}$; the authors of this study found this recovery time to vary greatly depending on the valley fill configuration of mining sites, but typically elevated levels of TDS and SC seemed to last for at least two to three decades (Evans et al., 2014). The aesthetics of receiving streams can be significantly affected if AMD is being produced from the mine

fills. Due to high concentrations of iron, AMD impaired waters can be characterized by an orange color. For the mine waters of southwestern Virginia, color is generally unaffected.

In terms of ecological impacts of increased TDS and SC, research has shown there is variability in effects based on the organism being studied. Studies that have examined benthic macroinvertebrates, such as ephemeroptera, plecoptera, and tricoptera, found a drop in “richness” in streams with high SC levels (Pond et al., 2008; Boehme, 2013). Seasonal variations have also been found to influence the severity of SC impacts on benthic macroinvertebrates (Boehme, 2013). However, studies that have tested the toxicity of TDS exposure of up to approximately 2,000 mg/L on juvenile rainbow trout found the high TDS exposure had little to no effect on survivability; the same study also examined chironomid larvae and found these organisms to more impacted in terms of survivability by TDS exposure in excess of 1,000 mg/L (Chapman et al., 2000). Daniels et al. (2014) suggest that the dominant ions present in high TDS waters influence toxicological response on benthic macroinvertebrates. Among the major constituents of TDS, sulfate has been identified as a possible indicator of biological health of mine impaired waters (Timpano et al., 2010).

Treatment Technologies

Mining effluent treatment technologies are typically categorized as either active, passive, or hybrid. Active systems have typically incorporated chemical and required long term maintenance. A system that consists of a lime-feed system leading to a settling pond would be considered an active system. Passive systems are designed to require less maintenance and investment for long periods of time. Some examples of passive systems include anoxic limestone drains, open limestone channels, constructed wetlands, successive alkalinity producing systems, and sulfate reducing bioreactors. A decision-making model have been developed in order to select passive treatment technologies that are best suited to the water quality present at a mining site; the main water quality parameters used differentiate passive treatment technologies are pH, dissolved oxygen (DO), ferric iron concentrations, and aluminum concentrations (Skousen and Ziemkiewicz, 2005). Due to varying levels of energy demand, membrane technologies are typically not included as a passive treatment option in these decision-making models. Passive systems have been successfully implemented in mining operations to mitigate the effects of AMD

(Skousen and Ziemkiewicz, 2005). Hybrid systems are designed to utilize principles from both active and passive treatment systems in order to optimize treatment performance; these systems are less common and more tailored to individual mining operations.

The performance of membrane technologies and biological sulfate reduction reactors has not been well documented for mining operations with effluent water quality similar to that of southwestern Virginia. Most studies examining the use of membrane technologies and sulfate reducing bioreactors have applied these technologies to AMD and other non-coal mine-impaired waters; specific conductivity removal performance is typically not included in treatment evaluation as well, which provides a significant gap of knowledge. The goal of this study is to evaluate membrane technologies and sulfate reducing bioreactors at the lab scale in terms of their ability to reduce SC and TDS levels found in coal mine impaired waters characteristic of southwestern Virginia; these technologies will be evaluated based on their ability to meet the SC upper benchmark of 500 $\mu\text{S}/\text{cm}$ as recommended by Cormier et al. (2011).

Membrane Technologies

Membrane treatment technologies involve forcing water being treated through a semipermeable membrane filter. The pore sizes of the semipermeable membrane filter are the differentiating factor across membrane treatment technologies. Membrane treatment technologies are commonly used in the desalination of high saline water and wastewater treatment while being coupled with activated sludge systems. Since this is a non-traditional technology when treating mine-impaired waters, most passive treatment decision making models fail to include membrane technologies as potential solution for treatment (Skousen and Ziemkiewicz, 2005). The removal mechanism will differentiate depending on the membrane type as well. The following are the common membrane technologies from largest to smaller pore size: microfiltration, ultrafiltration, nanofiltration, and RO. RO will not be considered in this study due to prohibitive operational costs related to pressure demands as high as 1,200 psi (Edzwald, 2011).

Table 2-1 lists the size of particles removed by each of the aforementioned membrane filters. Microfiltration and ultrafiltration systems are typically used a pretreatment to mitigate the effects of fouling on downstream treatment systems. Microfiltration membranes are able to remove bacteria and colloids; ultrafiltration

membranes are able to remove viruses and some dissolved organics (Edzwald, 2011). Due to their larger pore sizes, microfiltration and ultrafiltration systems are unable to remove most dissolved particles found in mine-impaired waters.

Table 2-1. Summary of particle sizes removed by each membrane (Adapted from Edzwald, 2011).

Membrane	Size of Particles Removed (μm)
RO	< 0.001
Nanofiltration	0.001 – 0.005
Ultrafiltration	0.005 – 0.12
Microfiltration	0.08 – 1.2

Nanofiltration membranes are characterized by having pore sizes less than 2 nanometers. Unlike microfiltration and ultrafiltration, nanofiltration is able to remove aqueous salts and some metal ions (Awadalla and Kumar, 1994). Nanofiltration systems utilize the following removal mechanisms in order to remove dissolved ions: electrostatic interactions between membrane and dissolved ions, sieving, and dielectric repulsion (Košutić et al., 2004). One advantage that nanofiltration systems have over RO systems is that they require lower pressures to achieve effective removal of some pollutants (Sierra et al. 2013). A concern for using nanofiltration, and other membrane technologies, is that they have variable removal efficiencies depending on the metal ion (Bolisetty and Mezzenga, 2016).

The influent in membrane systems can be forced through the membrane by either applied pressure or a vacuum. Temperature of the influent should be considered when designing membrane systems. Vacuum membrane systems struggle to filter colder influent due to its increased viscosity, which increases the force and power requirement needed to filter the sample. The three most common configurations of membrane treatment technologies are the dead-end, hollow fiber, and crossflow configurations. In the dead-end configuration, the influent is pressurized to flow perpendicular to the membrane surface. Dead-end filtration systems are prone to a buildup of rejected particles on the membrane surface, which can negatively impact the efficiency of the filtration system. In the hollow fiber configuration, the influent is collected into a series of semipermeable tubes to be filtered; like the dead-end configuration, hollow fiber membranes can either be pressure applied or vacuumed. In the crossflow configuration, influent continuously flows along

the surface of a membrane and allows the influent tangentially through the membrane; due to the continuous flow along the membrane surface, these systems have less issues with scaling (Awadalla and Kumar, 1994).

Membrane technologies offer a number of advantages and disadvantages as a potential treatment option. The main advantage of non-RO membrane technologies is that they are able to treat influent at low pressures, which can decrease operating costs of the system; a pretreatment stage should be included when there are solids greater than 0.1 mm in size in order to prevent damage to the membrane and to optimize system performance (Pinto et al., 2016). Nanofiltration, in particular, are able to operate at higher flux values when compared to RO and are able to remove multivalent anions and organic matter (Diawara, 2008). Fouling is another concern in regards to long term performance of membrane technologies. Due to the charged nature of the polymers used on the membrane, the pH of the water being treated could impact the performance of a nanofiltration system (Zhong, et al., 2007).

Fouling is an important consideration during the operation of membrane treatment technologies. One type of membrane fouling that can occur is scaling, which happens when rejected salts and precipitates accumulate on the membrane surface and block pores. The effect of the scaling depends on the accumulated species on the membrane surface; in some cases, some accumulated species are easily removed from backwashing (Rieger et al., 2009). Scaling effect has been observed in membrane studies examining mine-impaired waters; this study has suggested that the precipitation of calcium sulfate, or gypsum, during operation as a source of scaling (Al-Zoubi et al., 2010). Not only does scaling decrease the efficiency of the membrane system, but it can also damage the system and lead to increased maintenance costs (Visser et al., 2001). Fouling can be monitored in membrane filtration systems by measuring flux, which is modeled by equation 2-1. The flux of the membrane system typically decreases over time as the system experiences membrane fouling. Sarkar et al. (2011) found that the point at which scaling occurs directly correlated to the operating pressure and the influent flowrate of the system. Establishing optimum operating conditions, in terms of pressure and flowrate, is critical in order to prevent operating costs from becoming prohibitory for selection as a possible treatment option. Different techniques can be used to mitigate fouling in a membrane filtration

system, which include backwashing with water and backwashing with chemicals that can oxidize accumulated particles on the membrane surface.

$$J = Q/A_M \tag{2-1}$$

Compared to other technologies, there are not many studies involving the utilization of membrane technologies to treat coal mining effluent. Of the three membranes discussed, nanofiltration has been the most heavily investigated non-RO membrane technology for the purpose of treating mine-impaired waters. Table 2-2 summarizes reported removal levels for common ions found in coal mine-impaired waters of southwestern Virginia.

Table 2-2. Summary of pre-/post-treatment ion levels after nanofiltration.

Study	SO₄²⁻ (mg/L)	Mg²⁺ (mg/L)	Ca²⁺ (mg/L)	Na⁺ (mg/L)
<i>Al-Zoubi et al. 2010</i>	13,360 / 214	559 / 2.80	303 / 1.82	12.3 / 1.27
<i>Košutić et al. 2004</i>	134 / 0.386	N/A	N/A	N/A
<i>Ricci et al. 2015</i>	20.23 / 10.40	2429 / 277	423 / 91	N/A
<i>Rieger et al. 2009*</i>	14,337 / 287	631 / 13	326 / 7	N/A
<i>Sierra et al. 2013</i>	2,360 / 283	N/A	N/A	N/A
<i>Visser et al. 2001**</i>	1,430 / 14	N/A	354 / 11	344 / 17

*Post treatment concentrations were estimated based on reported removal rates

**Rejection values for NF70 used to estimate post-treatment concentrations

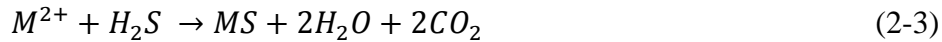
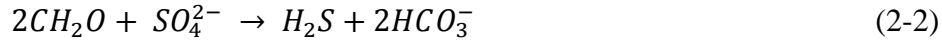
Al-Zoubi et al. (2010) explored the potential of nanofiltration for treatment of copper mining AMD instead of active treatment techniques; in this study, three different types of nanofiltration membranes were tested: NF99, DK, and GE. This study used a continuous cross-flow configuration to examine performance of each of the individual membranes being tested; each membrane was evaluated at two different pressures: 20 and 30 bar. Of the three membranes examined in this study, the NF99 and DK filters were consistent in performance in terms of ion removal for both pressures tested. Košutić et al. (2004) explored treating waters that had high levels of sulfate using various types of nanofiltration membranes, including the NF270; results showed that the nanofiltration membranes used in the study could remove greater than 94.5 percent of sulfate from the influent prescribed to the system. Ricci et al. (2015) used nanofiltration as a pretreatment stage prior to RO treatment of gold mining impaired waters; an additional microfiltration step was included prior to nanofiltration in order to allow for additional pretreatment. Unlike the waters characteristic of southwestern Virginia coal mine impaired waters, the

water being tested in this study had low sulfate concentrations and elevated levels of multivalent cations; the nanofiltration stage was able to remove at least 79 percent of all multivalent cations examined except for arsenic. Rieger et al. (2009) examined the treatment of copper mine effluent using two different types of nanofiltration membranes. Reported removal levels of ions present in southwestern Virginia coal mine impaired waters all exceeded 80 percent removal, with most ions removed in excess of 95 percent. In terms of fouling, Rieger et al. (2009) was able to identify gypsum and various metal hydroxides accumulating on the surface of the membranes after long-term system performance. Sierra et al. (2013) evaluated the use of nanofiltration in treating mercury mining effluent with the following ions of major concern: Al, Fe, As, and SO_4^{2-} ; removal of these ions was measured for pressures ranging from five to 30 bar in five bar intervals. Based on the data, as pressure of the system was increased, the concentrations of the ions in the permeate decreased; this indicates determining an optimal operating is important in order minimize the energy requirement costs in order to apply the pressure to the system. Visser et al. (2001) used a dead-end membrane configuration to use nanofiltration to treat gold mine effluent; the following types of nanofiltration membranes were used to treat the mine effluent: D11, D12, NF90, NF70, and CTC1. This study found that sulfate removal using membranes depended on the pH of the influent sample being tested; depending on which membrane was tested, sulfate removal would decrease as the pH of sample being tested decreased. Visser et al. (2001) found the NF70 and NF90 to provide the most comprehensive ion removal for the ions being examined, which included SO_4^{2-} , Cl^- , Na^+ , and Ca^{2+} .

Biological Sulfate Reduction

Sulfate reducing bioreactors are designed to operate similarly to a conventional activated sludge wastewater treatment system. Typically, sulfate reducing bioreactors combine a mixture of organic materials, such as compost, in order to encourage biological growth. These systems take advantage of biochemical reactions in order to reduce sulfate levels and precipitate any metals found in mine-impaired waters. Traditional passive treatment decision making models suggest the use of sulfate reducing bioreactors when dealing with mine-impaired waters that are acidic, have low DO concentrations, and have high iron and aluminum concentrations (Skousen and Ziemkiewicz, 2005).

Sulfate reducing bioreactors take advantage of various sulfate reducing bacteria in order to provide adequate treatment of mine impaired waters. Two common sulfate reducing bacteria in these systems are *Desulfovibrio vulgaris* and *Desulfovibrio sp.* (Cabrera et al., 2006). The main biochemical reactions of sulfate reducing bioreactors can be modelled by the following equations:



Equation 2-2 represents the reduction of sulfate with organic matter (CH₂O) serving as the oxidant; bicarbonate produced in this reaction will increase alkalinity in the system. Sulfate reducing bacteria require anaerobic conditions and the absence of metal oxidants in order for this reaction to occur (Hedin et al., 1994). Equation 2-3 represents the precipitation of metal sulfides that occurs when metals and hydrogen sulfide are present in the system. *Bowell (2004)* found that metal sulfide precipitation is optimized when the pH of the system is either neutral or slightly alkaline. Further precipitation reactions can occur if iron and aluminum are present in the system, which is typical in AMD water samples. Problems can occur in sulfate reducing reactors when the system becomes exposed to oxygen. When this occurs, it can have toxic effects on the sulfate reducing bacteria in the system and can proliferate aerobic bacteria which can produce unwanted reactions (*Hiibel et al., 2008*). Other than oxygen, the presence of nitrite in the system can also affect sulfate reducing bacteria's ability to reduce sulfate (*van den Brand et al., 2015*). In order to ensure anaerobic conditions are present in the system, oxidation-reduction potential (ORP) is typically measured; sulfate reducing bacteria have been found to proliferate when ORP is less than -100 mV (*Vasquez et al., 2016*). Another way to ensure suitable conditions for sulfate reducing bacteria is by calculating the COD/SO₄²⁻ ratio of the system; a common range of COD/SO₄²⁻ ratios for sulfate reducing bacteria is 0.7 to 1.5 (*Hao et al., 1996*). Critics have argued since COD is measured under aerobic conditions, the substitution of dissolved organic carbon (DOC) for COD would allow people to better understand the carbon supply available to sulfate reducing bacteria (*Neculita and Zagury, 2008*).

Like wastewater treatment systems, sulfate reducing bioreactors can be built in different configurations; *Kaksonen and Puhakka (2007)* outlines the variety of configurations for both passive and active sulfate reducing bioreactors. Sulfate reducing

bioreactors can be designed as both batch and continuous flow systems; batch systems are typically only used in laboratory applications, while continuous flow systems are more common in practice. In terms of passive configurations, Kaksonen and Puhakka (2007) identified infiltration beds, anoxic ponds, and wetland systems as possible configurations; each of these technologies rely on gravity to carry the mine impaired water through a zone where sulfate reducing bacteria are present. In terms of active configurations, the following systems were identified by Kaksonen and Puhakka (2007): sequencing batch reactors, continuously stirred tank reactors, anaerobic contact processes, anaerobic filters, fluidized-bed reactors, anaerobic hybrid reactors, and membrane bioreactors; these systems typically require an external energy source to pump water through the system and can have increased operational costs compared to passive systems.

During the design of sulfate reducing bioreactors, there is flexibility when considering potential materials to be used as media within the reactor. Generally, reactor media consists of the following components: bacteria source, pH neutralizer, nitrogen source, porous media, and carbon sources (Cocos et al., 2002). Limestone, urea, and sand are traditionally selected as a pH neutralizer, nitrogen source, and porous media for sulfate reducing bioreactors, respectively. Carbon sources used in sulfate reducing bioreactors are broken into the following two categories: organic and cellulosic. Both organic and cellulosic carbon sources are included in sulfate reducing bioreactors in order to provide the sulfate reducing bacteria short-term and long-term supplies of carbon and ensure successful sulfate reduction (Neculita et al., 2007). Selection of organic and cellulosic carbon sources allows for the incorporation of locally sourced materials. Common materials selected for cellulosic carbon sources include: sawdust, alfalfa hay, wood chips, and mulch; manure and compost are typically selected as the organic carbon source for sulfate reducing bioreactors (Gusek, 2002). Table 2-3 summarizes the different mixtures used in sulfate reducing bioreactor studies that produced optimal results; if the study used multiple different reactor mixtures, the reactors with the highest ion removal levels were reported in this table. In order to ensure effective long-term performance of sulfate reducing bioreactors, an external carbon source such as ethanol can be added to the system to stimulate performance as the original sources of carbon of the system become exhausted (Tsukamoto et al., 2004).

Table 2-3. Summary of BSR mixtures by percent dry weight.

Component	Cocos et al. 2002	Neculita & Zagury 2008	Hiibel et al. 2008	Vasquez et al. 2016
<i>Bacteria Source</i>	Sediment (37%)	Sediment (15%)	N/A	Sediment (15%)
<i>Nitrogen Source</i>	Urea (3%)	Urea (3%)	N/A	N/A
<i>Porous Media</i>	Sand (5%)	Sand (30%)	N/A	Gravel (20%)
<i>pH Neutralizer</i>	Limestone (2%)	Limestone (2%)	Limestone (29%)	Limestone (15%)
<i>Organic Carbon Sources</i>	Poultry Manure (20%)	Composted Poultry Manure (10%)	Dairy Cow Manure (10%)	Cow Manure (15%)
	Leaf Compost (30%)	Leaf Compost (20%)		Mushroom Compost (10%)
<i>Cellulosic Carbon Sources</i>	Woodchips (3%)	Woodchips (10%)	Woodchips (10%)	Sawdust (25%)
		Sawdust (20%)	Alfalfa Hay (10%)	
			Kiln Dust (1%)	

*N/A indicates information was unavailable

Sulfate reducing bioreactors offer multiple advantages for mining operations. Some of advantages of sulfate reducing bioreactors include minimal maintenance, built-in reuse of hydrogen sulfide and carbon dioxide, and the ability to remove trace metals from the influent (Bowell, 2004). Another advantage of sulfate reducing bioreactors is that they are resilient in terms of being able to handle varying influent conditions; they are able to handle fluctuations in water quality well (Gusek, 2002). As mentioned earlier, sulfate reducing bioreactors are able to be designed to incorporate organic materials, such as compost and wood chips, that are easily obtained near mining operation sites. Depending on the configuration of the system, passive sulfate reducing bioreactors provide a relatively inexpensive treatment method of mine impaired waters (Gusek, 2015); this is especially true when compared to membrane technologies.

There are several potential concerns for mining operations to consider involving sulfate reducing bioreactors. A major concern of sulfate reducing bioreactors is the potential of hydrogen sulfide gas formation; not only does this present an on-site safety issue, but it may create odor issues for nearby inhabitants (Rose, 2010). Long startup times

for a sulfate reducing bioreactor are another concern mining operations would need to consider; depending on the scale of the system, it may take months for the bacteria to become acclimated (Rose, 2010). This concern can be mitigated by utilizing an inoculum bacterial source during the reactor’s startup. Plugging and clogging of reactors are also a concern when metal sulfide precipitates accumulate within the system; this usually isn’t an issue if the bioreactor is designed properly (Tsukamoto et al., 2004; Gusek 2015). Variations in temperature can impact the effectiveness of sulfate reducing bioreactors due to the fact that sulfate reducing bacteria don’t function properly at colder temperatures (Behum et al., 2011; Gusek, 2002). Sulfate reducing bioreactor also has the potential to have elevated biochemical oxygen demand (BOD) levels in its effluent which isn’t typically monitored under most mining NPDES permits (Gusek, 2015). For the design of passive sulfate reducing bioreactors, there is not a standardized design when it comes to producing effective treatment of mine impaired waters (Figueroa et al., 2007). This is evident when examining the multiple mixtures tested in bioreactors (Cocos et al., 2002; Neculita and Zagury, 2008; Vasquez et al., 2016).

Sulfate reducing bioreactors have been applied to various mining operations with varying levels of success depending on which parameter is used to evaluate the system; these systems are commonly used to treat mine impaired waters where AMD is a primary concern. A summary of the reported pre- and post-treatment ion concentrations of sulfate reducing bioreactor studies can be found in Table 2-4.

Table 2-4. Summary of pre-/post-treatment ion levels after BSR.

Study	SO₄²⁻ (mg/L)	Mg²⁺ (mg/L)	Ca²⁺ (mg/L)	Na⁺ (mg/L)
<i>Behum et al. 2011</i>	2981 / 1750	N/A	N/A	N/A
<i>Cocos et al. 2002</i>	2940 / <90	N/A	N/A	N/A
<i>De Vegt et al. 1998</i>	30000 / <500	4500 / 1950	480 / 50	N/A
<i>Hübel et al. 2008*</i>	988 / 366	N/A	N/A	N/A
<i>Neculita and Zagury 2008</i>	5500 / 0	N/A	N/A	N/A
<i>Vasquez et al. 2016</i>	2345 / 539	N/A	N/A	N/A

*Post treatment concentrations were estimated based on reported removal rates

Behum et al. (2011) monitored the performance of a sulfate reducing bioreactor treating from AMD effluent from a coal mine in Illinois. This study found that sulfate removal rates varied depending on the season, with summer conditions achieving elevated

removal rates. Cocos et al. (2002) evaluated 17 different reactor mixtures for treating a synthetic AMD; each mixture used the same basic components within a batch reactor configuration, however the percentage of each component was varied for each mixture. The reactors in this study required an approximate 21-day incubation to develop suitable conditions for sulfate reducing bacteria and was able to reach effluent sulfate levels below 90 mg/L in 41 days. In de Vegt et al. (2008), an upflow anaerobic sludge blanket (UASB) system was utilized to treat groundwater with elevated sulfate levels; the full treatment plant included the following stages: UASB, submerged fixed-film reactor, plate settler, and a sand-bed filter. The water treatment examined proved to be effective in terms of sulfate removal, as well as precipitation of multivalent metal cations as metal sulfides. Hiibel et al. (2008) examined the microbial community of two pilot-scale sulfate reducing bioreactors that were treating AMD; one of the reactors in this study was found to contain aerobic bacteria which was cited as a reason the reactor had lower removal rates compared to the reactor that was reported in Table 2-4. Neculita and Zagury (2008) tested the performance of three different mixtures in order to determine which was best for treating AMD mine effluent. The batch reactors required at least 80 days before any sulfate reduction occurred, but once the bacteria were acclimated in the batch reactors sulfate removal rates above 90 percent were obtained. Vasquez et al. (2016) tested five different mixtures for a sulfate reducing bioreactor in an effort to treat AMD. In terms of sulfate removal, all of the mixtures tested required at least 30 days before sulfate reduction occurred. Since this study used a continuous flow configuration, permeability of the mixture was a major concern in order to prevent clogging of the system.

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Chapter 3 – MEMBRANE TECHNOLOGIES

REDUCTION OF SPECIFIC CONDUCTIVITY IN COAL MINE EFFLUENT USING MEMBRANE TECHNOLOGY

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Abstract. Recent studies have found a correlation between specific conductivity (SC) and total dissolved solids (TDS) and health of aquatic organisms in receiving streams near coal mine valley-fill structures. Due to the potential for regulation demanding limits on SC and TDS, coal mining operations have begun to explore treatment technologies that could be used to mitigate SC and TDS in receiving streams. Nanofiltration was evaluated based on its ability to reduce SC and meet a proposed limit of 500 $\mu\text{S}/\text{cm}$ for mine water samples with moderate and high levels of SC. Three nanofilters (NF270, DK, NFX) were tested without any pretreatment in the first phase of this project. The DK and NFX nanofilters were able to meet this SC limit for both mine waters tested with an average reduction of 84 percent for both mine waters tested. The NF270 nanofilters tested had an average SC reduction of 69 and 59 percent for the moderate and high SC mine waters tested, respectively. Performance in terms of SC reduction declined as ion concentrations increased in the influent tested. In the second phase of this project, microfiltration and simulated-sand filtration were introduced as a pretreatment stage in order to determine if SC reduction could be enhanced. Upon experimentation, neither of the pretreatment options improved SC reduction accomplished by nanofiltration.

Additional Key Words: microfiltration; nanofiltration; specific conductance; sulfate; total dissolved solids; ultrafiltration; valley-fill.

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Introduction

Coal mining operations are traditionally only regulated on the following water quality parameters under the Surface Mining Control and Reclamation Act (SMCRA) and the Clean Water Act (CWA): pH, iron, and total suspended solids (TSS). In recent years, the US Environmental Protection Agency (EPA) has recommended a regulatory effluent limit on specific conductance (SC) of 500 $\mu\text{S}/\text{cm}$ based on a recent study that examined the correlation between SC and aquatic health in mine impaired waters (Cormier et al., 2011). Other studies have found that elevated SC levels can negatively impact benthic macroinvertebrates which are typically used as aquatic health indicators (Pond et al., 2008; Boehme, 2013). In particular, elevated sulfate (SO_4^{2-}) concentrations in receiving streams has been identified to have detrimental effects on aquatic species (Timpano et al., 2010). Ultimately no SC limit was established, but there is concern in the coal mining industry that an effluent regulation could be on the horizon.

Both SC and total dissolved solids (TDS) are measures of the ionic makeup of a solution. The common ions that contribute to SC and TDS in mining impaired waters include the following: SO_4^{2-} , calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) (Orndorff et al., 2010). If the mine impaired waters are considered acid mine drainage (AMD), high concentrations of iron and aluminum can also be present; the coal mine waters of southwestern Virginia would not be considered AMD. In both AMD and coal mine impaired waters of southwestern Virginia, sulfate has the highest ionic presence in solution (Merovich et al., 2007). TDS can be calculated from the SC value based on a determined ratio; this ratio can range from 0.5 to 1.0 (Oram, 2014). In order to determine this relationship, TDS must be quantified for the test sample of a predetermined SC value using a standardized method.

Traditionally, mining operations have utilized active treatment technologies that employ chemical addition in order to precipitate metals and raise pH. Due to prohibitive costs related to active chemical addition systems, passive systems are becoming increasingly popular as a treatment method of mining impaired waters. Decision making models have been developed in order to select a passive treatment technology best suited to treat a site based on its water quality characteristics (Skousen and Ziemkiewicz, 2005); the water quality characteristics typically used to choose a suitable passive treatment

technology include pH, dissolved oxygen (DO), and ferric iron and aluminum concentrations. SC and TDS remain absent from these models, leaving a knowledge gap for the effectiveness of each technology in regards to SC and TDS removal.

Membrane technologies are increasingly being examined as possible treatment solutions for mining operations despite not being a truly passive treatment technology. The most common membrane technologies from smallest pore size to largest pore size are: reverse osmosis (RO), nanofiltration, ultrafiltration, and microfiltration. Microfiltration and ultrafiltration are typically used as pretreatment option for removing larger particles that could negatively impact downstream treatment processes (Awadalla and Kumar, 1994). These membranes are able to remove the following: bacteria, viruses, colloids, and some dissolved organics (Edzwald, 2011). RO has been proven to be effective in removing dissolved ions, however was not considered in this study due to the high operational costs associated with its pressure requirement that can reach pressures as high as 1,200 psi (Edzwald, 2011).

Like RO, nanofiltration is a membrane technology that is able to remove certain dissolved ions (Awadalla and Kumar, 1994). When compared to RO, nanofiltration is able remove dissolved ions at much lower operating pressures, which decreases a system's operating costs (Pinto et al., 2016); nanofiltration systems are also able to operate at higher fluxes than RO systems (Diawara, 2008). One of the major concerns with membrane technologies is fouling. Scaling, a form of fouling, occurs when solids build up on the membrane surface and block pores, thus negatively impact system performance. The type of residual formed on the membrane surface will vary depending on the influent water quality. Due to decreased treatment efficiency over time, scaling can lead to system damage and may require maintenance that would increase costs for the system (Visser et al., 2001). Another concern with nanofiltration is that the reduction of ions within a sample varies depending on the complexity of the sample (Bolisetty and Mezzenga, 2016); this could be a potential performance issue when dealing with complex mine waters.

Nanofiltration has been proven to be a capable option for the reduction of common ions that are characteristic of the coal mining impaired waters of southwestern Virginia. Several studies have applied nanofiltration to treat AMD from various types of mining effluent (Al-Zoubi et al., 2010; Košutić et al., 2004; Ricci et al., 2015; Rieger et al. 2009;

Sierra et al., 2013; Visser et al. 2001). Excluding Visser et al. (2001) where SO_4^{2-} concentrations were low, nanofiltration was able to achieve at least 88 percent SO_4^{2-} reduction in each of the previously mentioned studies; the remaining major ions found in coal mine waters of southwestern Virginia were effectively reduced as well.

The goal of this study was to test the feasibility of using various nanofiltration membranes to reduce SC and TDS levels in coal mining impaired waters that are characteristic of southwestern Virginia. In order to evaluate each membrane experiment, the resulting SC value of each treatment was compared to the proposed upper limit of 500 $\mu\text{S}/\text{cm}$, as recommended by Cormier et al. (2011). The ionic makeup of the filtrate from each treatment was compared to that of the source water in order to understand which ions were better removed. Microfiltration and simulated-sand filtration pretreatment stages were also tested to determine whether or not they would improve treatment by nanofiltration.

Materials and Methods

Samples were collected from two mine-impaired streams located in southwestern Virginia. The two selected streams emanated from active, valley-fill structures that utilize different design principles. These streams were selected because they were known to have different levels of SC; this would allow for the testing of both moderate and high SC level water samples. The Office Fill (OF) samples were collected in a stream originating from a conventional, valley-fill structure. The stream travels through rocky outcrops and over a gravel service road. The Barton Hollow (BH) samples were collected from a valley-fill structure that utilizes an experimental system designed to lower SC levels. Experimental systems are designed to only incorporate mining materials known not to generate high level of SC and TDS, as well as design features intended to minimize infiltration into the valley-fill structure. After leaving the valley-fill structure, the BH stream follows a well-developed stream bed that is densely vegetated and eventually flows to a settling pond. The collection of samples for each site was completed on separate days during the summer of 2016. For the OF site, samples were collected at a point where the stream crossed over a gravel service road and dropped into a stream. For the BH site, samples were collected

after a period of rainfall; samples were collected near a flume located upstream from the aforementioned settling pond.

A stirred cell system (Sterlitech HP4750) was used to conduct membrane testing; this system is a dead-end configuration membrane apparatus that utilizes direct pressure to force the influent water sample through the system (Figure 3-1). The stirred cell system could hold a maximum of 300 mL of sample at a time. Compressed nitrogen gas was used as the pressure source. A graduated cylinder was used in order to capture the filtered water sample and to monitor the progress of the filtration process.

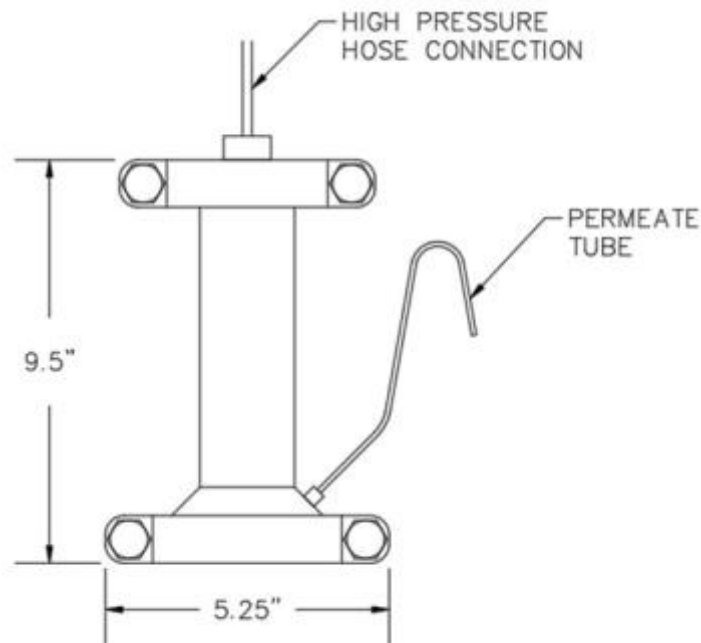


Figure 3-1. Basic drawing of the Sterlitech HP4750 Stirred Cell membrane apparatus.

For this study, multiple operating conditions were tested in order to identify the best treatment procedure. Initially, the mine water samples were tested using each type of nanofiltration membrane without a pretreatment stage. The characteristics of each nanofiltration membrane tested in this phase of the study is given in Table 3-1. In the second phase of testing, a pretreatment stage was incorporated prior to nanofiltration testing. Two pretreatment methods were examined: microfiltration and simulated sand filtration. For microfiltration, a TriSep TM10 microfiltration membrane was used to filter the mine water samples. In order to simulate sand filtration, a Whatman GF/B filter (1.0 μm) was used to filter each of the mine water samples (Edzwald, 2011). Once a prefiltered

sample was obtained for each water sources, tests were performed using one of the previously mentioned nanofiltration membranes; this nanofiltration membrane was selected based on the results of the first phase of testing in order to select for a membrane that would provide consistent results. The SC values measured after nanofiltration were statistically analyzed using Tukey’s multiple comparison test in order determine if SC values for each nanofilter tested. This statistical analysis was conducted using R statistical programming.

Table 3-1. Summary of Nanofiltration Membrane Characteristics (Adapted from Sterlitech, 2016).

Filter	NF270	DK	NFX
<i>Manufacturer</i>	Dow Filmtec	GE Osmonics	Synder Filtration
<i>Polymer</i>	Polyamide-TFC	Thin Film	Polyamide-TFC
<i>MWCO (daltons)*</i>	200 - 400	150 – 300	150 – 300
<i>pH</i>	2-11	2 – 10	3 – 10.5
<i>Flux (GFP/psi)</i>	(72-98)/130	22/100	(20-25)/110
<i>Flux (GFP/bar)</i>	(72-98)/8.96	22/6.89	(20-25)/7.58

*MWCO – Molecular Weight Cut-Off

For a given test, the selected membrane was placed in the filter support. Once in place, the apparatus was assembled as specified by the manufacturer. Prior to testing the mine water sample, 100 mL of nanopure water was added to the assembly to allow for the conditioning of the membrane being tested. During this conditioning step, the same operating pressure to be used during the filtration of the mine water sample was used for consistency. The conditioning step was continued until the water flux being monitored reached a steady-state. During the operation of the membrane apparatus, the water flux was monitored by tracking the volume of collected filtrate at specified time intervals until the entire system was completely filtered. The water flux was calculated using Equation 3-1:

$$J = Q/A_M \tag{3-1}$$

In order to complete this calculation, a timer was used to monitor the filtrate collected at specified time intervals. Using these data, the flow-rate (Q) of the system was determined, and the water flux was then calculated by dividing by the membrane’s surface area (A_M).

After membrane conditioning was completed, the apparatus was disassembled and 100 mL of the desired mine water sample was added. Once reassembled, the apparatus

was connected to the pressure source and the pressure regulator was set to the desired pressure. Eight bar (116 psi) was selected as the operating pressure for nanofiltration membranes for consistency based on the manufacturer's recommendation for optimal operational flux. Once the pressure valve was opened and the first droplet of filtrate fell into the graduated cylinder, a timer was started. Every five minutes, the amount of filtrate present in the graduated cylinder was recorded in order to calculate the water flux. During the operation of the apparatus, a magnetic stirrer (Benchmark Magnetic Stirrer) was set to a mid-range stirring rate. For each specific membrane test, the same individual membrane was used for three replicates. Between individual tests, the membranes were gently rinsed and soaked with nanopure water for at least 10 minutes.

The SC of the filtrate was measured using an Omega CDH-SD1 conductivity meter. SC to TDS ratios were determined by measuring the TDS of samples at the following SC ranges: 0-1,000 $\mu\text{S}/\text{cm}$, 1,000-2,000 $\mu\text{S}/\text{cm}$, and greater than 2,000 $\mu\text{S}/\text{cm}$. TDS was determined in accordance with Standard Methods 2540-C for five replicates from each of the specified SC ranges (Rice et al., 2012). This testing yielded the following SC to TDS ratios for the 0-1,000 $\mu\text{S}/\text{cm}$, 1,000-2,000 $\mu\text{S}/\text{cm}$, and greater than 2,000 $\mu\text{S}/\text{cm}$ ranges of 0.64, 0.83, and 0.95, respectively. Inductively coupled plasma – mass spectrometry (ICP-MS) was used to measure the concentrations of cations present in the source water and filtrate. Alkalinity was measured via the titration methodology using 0.02 N sulfuric acid as recommended by Standard Methods 2320-B (Rice et al., 2012). The pH of the filtrate samples was measured using a pH meter (Oakton acorn series, pH 6 meter). Turbidity was measured using a turbidimeter (Orbeco-Hellige digital direct-reading turbidimeter). All meters used in this study were calibrated weekly prior to testing.

A build-up of residual solids was expected to develop on the surface of the membrane during testing. Unrinsed NF270 filters after the treatment of BH water samples were submerged in 100 mL of nanopure water and agitated to get a better understanding of the residual solids that developed on the surface of nanofilters after operation. The samples collected were then vigorously shaken in order to promote the dissolving of the solids in solution. These samples were then analyzed by means of ICP-MS to better understanding of the ionic makeup of each sample. The dry weight of the residual solids in each sample

was quantified by drying 10 mL of each sample at a temperature range of 103°C to 105°C. The results of ICP-MS analysis were reported on a unit weight basis.

Results and Discussion

Characteristics of the mine-impaired waters examined in this study are provided in Table 3-2. Initially, each type of nanofilter was individually tested to treat samples from both water sources. In terms of SC reduction, Figure 3-2 displays the effluent SC levels achieved by each individual membrane for both influent water samples. For the BH water samples, both of the low-flux nanofiltration membranes (NFX and DK) were able achieve SC reductions below the proposed 500 $\mu\text{S}/\text{cm}$ limit. The NFX and DK nanofilters were able to achieve an average of 82 and 86 percent SC reduction, respectively. The NF270 nanofilter provided the least amount of SC reduction of the three nanofiltration membranes being tested at 69 percent. The NF270 nanofilter also had the highest variability in terms of SC reduction with a standard deviation of 155 $\mu\text{S}/\text{cm}$, while NFX and DK had standard deviations below 50 $\mu\text{S}/\text{cm}$. For the OF water samples, similar trends in terms of SC reduction were found. Both NFX and DK reduced SC on average of 83 and 85 percent, respectively, and were able achieve average SC levels below 500 $\mu\text{S}/\text{cm}$. When compared to the BH samples, the OF nanofilter results tended to have more variation in terms of standard deviation. In this respect, DK experienced the least amount of standard deviation at 77 $\mu\text{S}/\text{cm}$, while NF270 had a standard deviation of 246 $\mu\text{S}/\text{cm}$.

Table 3-2. Summary of Water Quality Characteristics.

Characteristics	Barton Hollow (BH)	Office Fill (OF)
SC ($\mu\text{S}/\text{cm}$)	1,534	2,505
TDS (mg/L)	1,273	2,380
pH	7.53	7.62
Alkalinity (mg/L as CaCO_3)	100	198
Turbidity (NTU)	7.19	12.90
SO_4^{2-} (mg/L)	776	1,380
Ca^{2+} (mg/L)	181	346
Mg^{2+} (mg/L)	93.6	247
Na^+ (mg/L)	22.8	36.0
K^+ (mg/L)	7.7	10.5

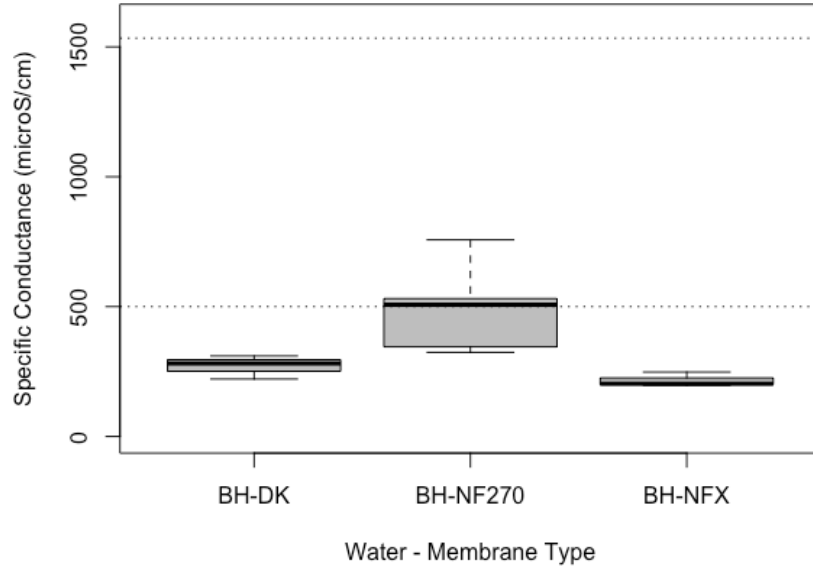


Figure 3-2. Filtrate SC levels after nanofiltration of BH water samples when compared to influent and targeted effluent SC levels.

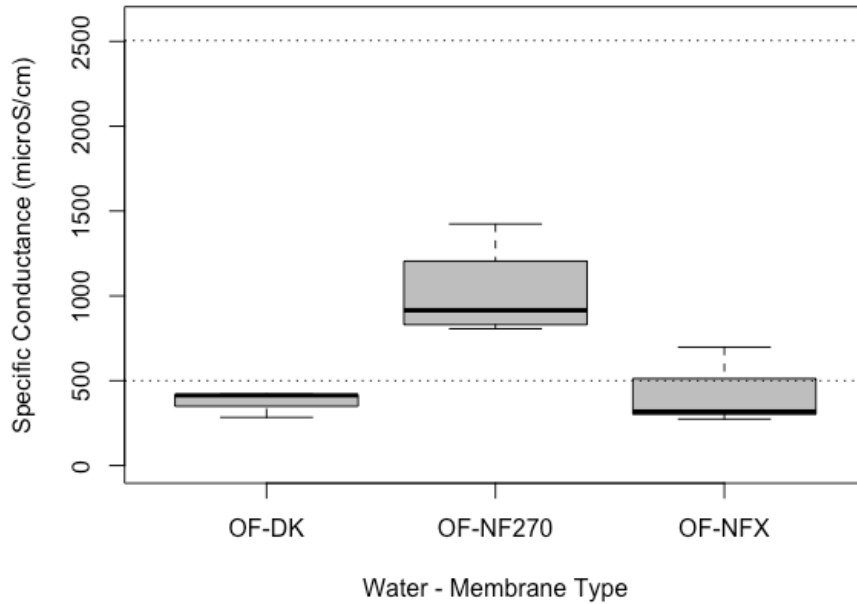


Figure 3-3. Filtrate SC levels after nanofiltration for OF water samples when compared to influent and targeted effluent SC levels.

In order to monitor membrane fouling, water flux was monitored during each membrane test. The average water flux for each membrane monitored over time can be seen in Figure 3-3. The water flux results followed similar trends to previous studies (Al-Zoubi et al., 2010). For all nanofilters tested, the water flux measured decreases during the performance of the membrane apparatus. This is most likely due to the accumulation of

solids on and within the membrane, which would impact the flowrate of the system and thus the calculated flux.

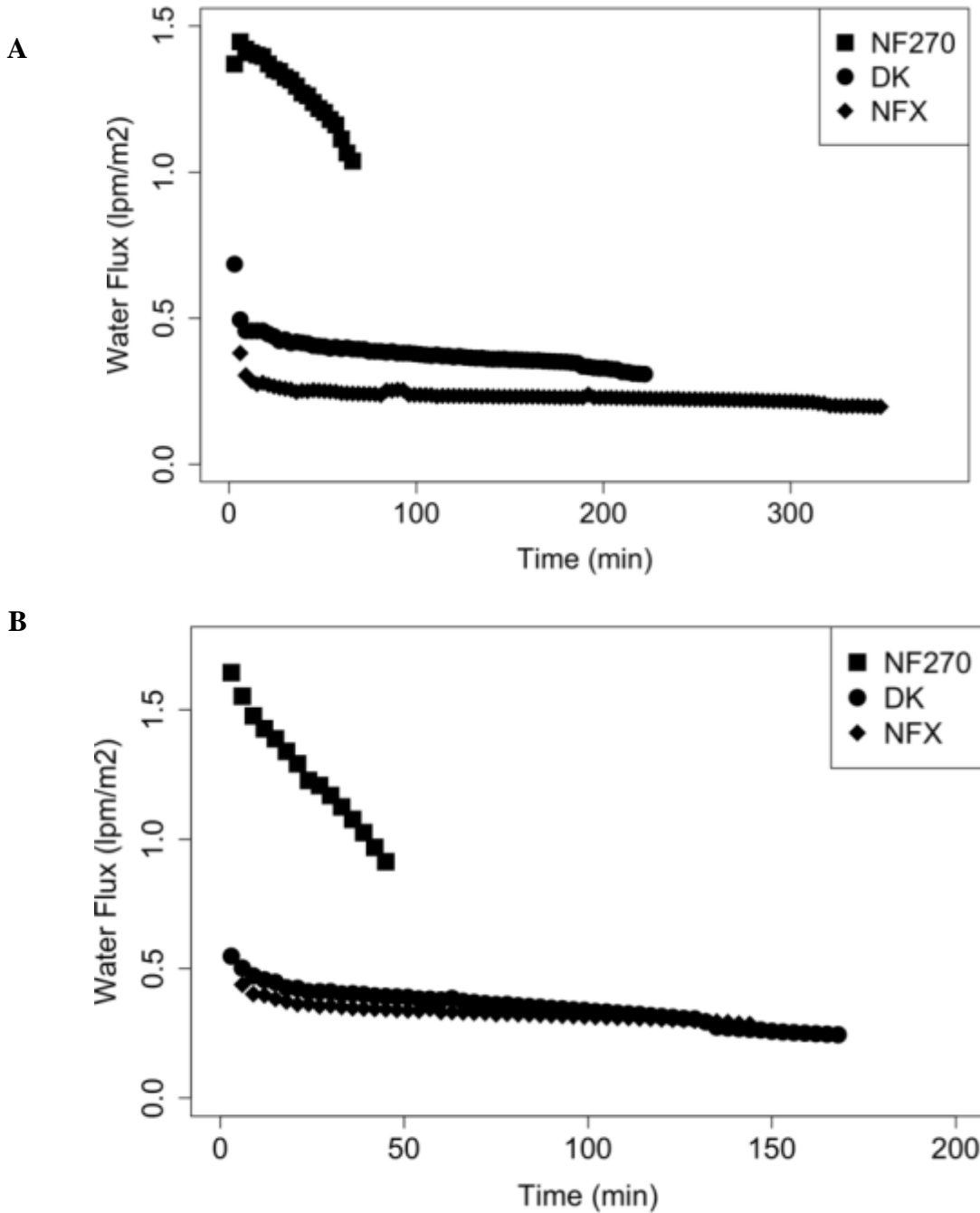


Figure 3-4. Water flux over time for (A) BH and (B) OF tests.

Table 3-3 provides the concentrations of ions measured in the filtrates of tests with each nanofilter. Each of the nanofilters performed well in terms of SO_4^{2-} reduction with the minimum reduction rate for all water samples at 77 percent. Average SO_4^{2-} reduction for

the testing conducted on BH water samples were 84, 94, and 98 percent for NF270, DK, and NFX, respectively. Average SO_4^{2-} reduction for the testing conducted on BH water samples were 84, 94, and 98 percent for NF270, DK, and NFX, respectively. Average SO_4^{2-} reduction for the testing conducted on OF water samples were 77, 96, and 94 percent for NF270, DK, and NFX, respectively. The divalent cations examined in this study, Ca^{2+} and Mg^{2+} , experienced similar average reductions to SO_4^{2-} which range from 71 to 96 percent. Of the cations and anions examined in this study, Na^+ and K^+ had the lowest average reduction for both mine waters tested. For BH test samples, the Na^+ and K^+ maximum average reduction rates among the three nanofilters tested were 40 and 45 percent, respectively. For OF test samples, the Na^+ and K^+ maximum average reduction rates among the three nanofilters tested were 37 and 45 percent, respectively. Of the three nanofilters tested, the NF270 had the highest Na^+ and K^+ reduction rates.

Table 3-3. Summary of phase I filtrate water quality characteristics.

Water Source	Nanofilter	No. of Rep. (n)	SC ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)
BH	NF270	7	477	324	122	37	25	14	4
BH	DK	3	271	180	43	14	11	19	8
BH	NFX	3	216	147	13	17	6	16	5
OF	NF270	7	1,031	783	311	78	71	22	6
OF	DK	3	373	253	50	13	17	26	7
OF	NFX	5	421	286	78	26	16	24	7

The SO_4^{2-} reduction rates achieved by NF270 nanofiltration treatment can be compared to those found by Košutić et al. (2004). Testing from Košutić et al. (2004) had a SO_4^{2-} reduction rate of 95 percent. This SO_4^{2-} reduction rate was greater than reached by using the NF270 to treat both BH and OF water samples. The results from DK testing can be compared to the those found by Al-Zoubi et al. (2010). Al-Zoubi et al. (2010) was able achieve SO_4^{2-} , Mg^{2+} , Ca^{2+} , and Na^+ reduction rates of 98, 99, 99, and 90 percent, respectively. These reduction rates were comparable to those achieved in this study, except for that found for Na^+ which was only able to reduce at a rate of 15 and 40 percent for BH and OF water samples, respectively.

Figure 3-5 shows how the residuals were typically deposited on the membrane apparatus and the membrane filter at the end of an experiment. The residuals deposited on

the membrane surface coated the part of the apparatus closest to the membrane. This residual remained on the surface of the membrane apparatus unless it was vigorously scoured. Very little residual on the membrane apparatus was able to be removed. As mentioned earlier, multiple studies identified gypsum as a common scalant in these systems (Al-Zoubi et al., 2010; Rieger et al., 2009). A significant amount of the residual from the membrane apparatus was unable to be obtained for further analysis in order to chemically identify the substance. Most of the solids on the surface of the membrane were easily removed by rinsing the membrane surface with water. The ions found in the residuals tested using ICP-MS can be found in Table 3-4. Based on the high SO_4^{2-} and Ca^{2+} reduction rates achieved by the NF270 nanofilter after treatment of BH water samples and the fact that these two ions have the highest concentrations in the influent, it makes sense that these ions would be accumulated on the surface of the membrane in the greatest concentrations.

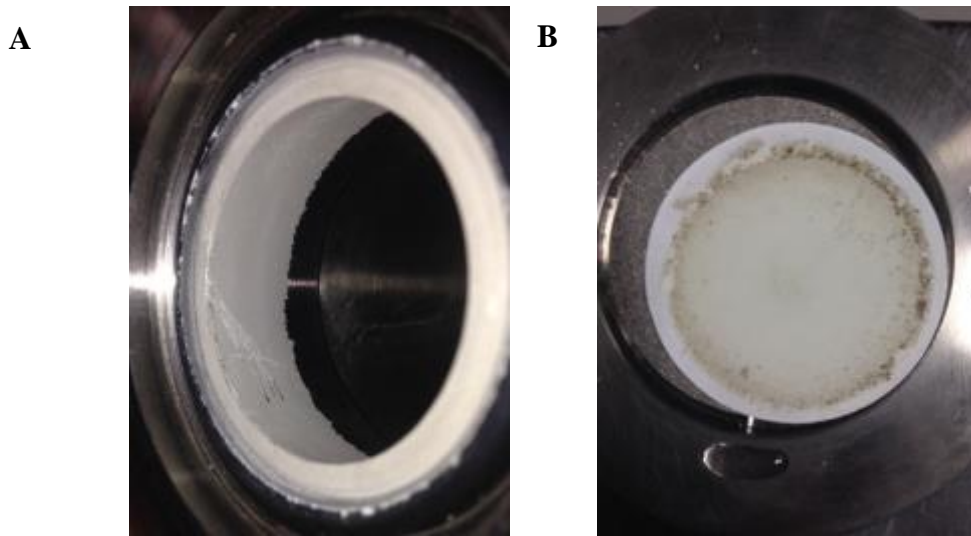


Figure 3-5. (A) Solids build up membrane apparatus and (B) solids accumulation on membrane surface.

Table 3-4. ICP-MS analysis of accumulated solids on DK membrane.

Sample	SO_4^{2-} (mg/mg)	Ca^{2+} (mg/mg)	Mg^{2+} (mg/mg)	Na^+ (mg/mg)	K^+ (mg/mg)
S1	0.471	0.156	0.023	0.005	0.003
S2	2.188	0.621	0.138	0.015	0.007
S3	0.816	0.272	0.032	0.004	0.002

The second phase of testing introduced one of two pretreatment options prior to direct nanofiltration testing: microfiltration and simulated-sand filtration. Initially, at least 300 mL of water sample were filtered using each of the pretreatment methods. Both pretreatment options provided minimal SC reduction to the tested influent samples; this was to be expected based on the previously reported kinds of molecules removed by microfiltration membranes (Edzwald, 2011). Even though the influent water samples tested already had mean turbidity levels below 15 NTU, both pretreatment options were able to reduce turbidity to levels achieved by nanofiltration in the first phase of nanofiltration testing. The type of nanofilter chosen to treat each of the pretreated samples was selected based on the performance of testing from the first phase of experimentation. The NFX nanofilter was selected for treatment of the pretreated samples due to its consistent results in terms of SC reduction.

Figures 3-6 and 3-7 depict the SC levels achieved by nanofiltration after each of the prescribed pretreatment steps. For the BH samples, each of the treatments were able to reduce SC lower than the 500 $\mu\text{S}/\text{cm}$ SC limit on average. When compared to the NFX treatment of BH water samples, only the samples microfiltered prior to nanofiltration were statistically different in terms of end SC level based on a multiple comparison test. The previously microfiltered samples had an average effluent SC level of 306 $\mu\text{S}/\text{cm}$, which was greater than both effluent SC levels obtained by the other testing conditions. For the OF samples, each of the treatments were not statistically different from the NFX samples collected without pretreatment in terms of end SC level based on a multiple comparison statistical analysis. Table 3-5 contains the mean characteristics of each of the filtered samples collected during this phase of experimentation.

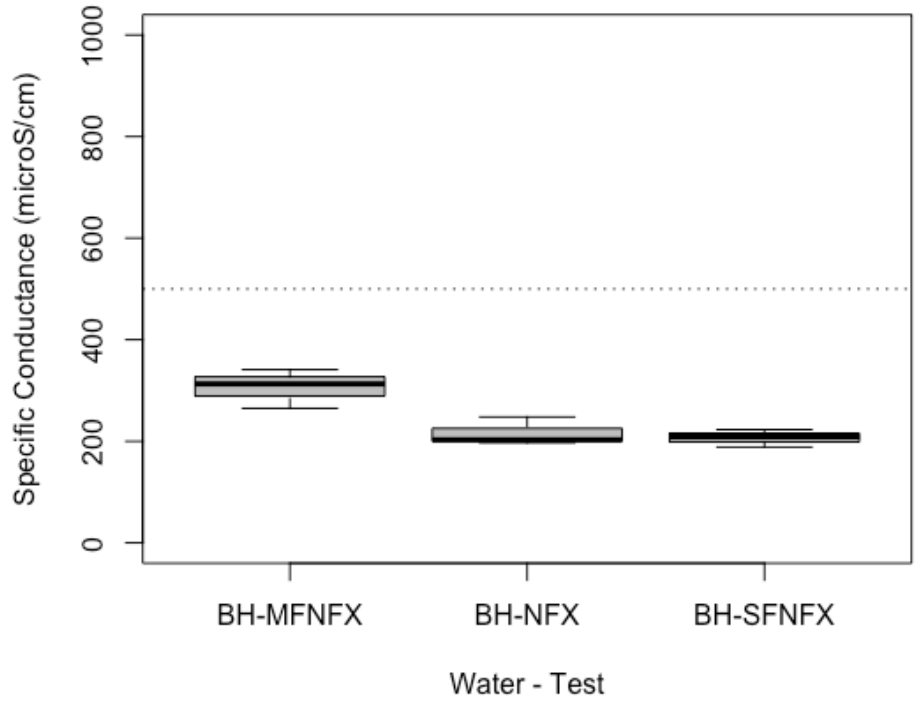


Figure 3-6. Nanofiltration of BH samples after pretreatment.

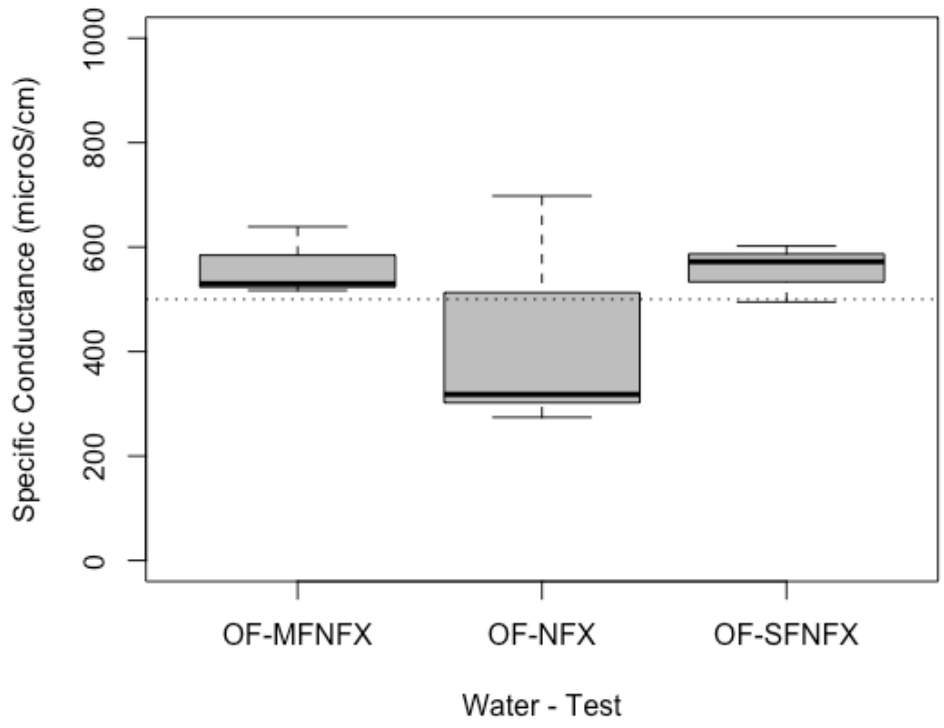


Figure 3-7. Nanofiltration of OF samples after pretreatment.

Table 3-5. Summary of phase II filtrate water quality characteristics.

Water Source	Test	SC (μS/cm)	TDS (mg/L)	SO ₄ ²⁻ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)
BH	SFNF	207	141	18	12	5	15	5
BH	MFNF	306	208	39	19	9	13	4
OF	SFNF	556	378	112	33	27	23	6
OF	MFNF	562	382	124	29	30	23	6

When compared to the effluent ion concentrations achieved by the NFX nanofilter in the first phase of this study, the ionic concentrations and associated reduction rates were comparable to those found when a pretreatment stage was incorporated prior to nanofiltration. For both testing conditions and water samples, SO₄²⁻ reduction rates all exceeded 90 percent. Like in the first phase of experimentation, Na⁺ and K⁺ reduction rates were the lowest among the ions measured. The average Na⁺ and K⁺ reduction rates for both testing conditions were between 30 and 40 percent.

Conclusions

At the lab scale, nanofiltration was shown to be a potentially effective treatment technology for SC reduction. Of the three nanofiltration membranes tested, the low-flux nanofilters (DK and NFX) on average were able to meet the potential 500 μS/cm SC limit for both mine waters tested. Each of these nanofilters were able to reduce SO₄²⁻ concentrations by at least 90 percent. The NF270 nanofilter experienced the greatest amount of variability of the three nanofilters tested. In general, as ion concentrations increased in the influent tested with the OF samples, variability of membrane performance increased. When a pretreatment stage of microfiltration or simulated-sand filtration was introduced prior to nanofiltration was introduced, increased performance in terms of SC reduction was not achieved.

Further testing will be required to determine whether or not nanofiltration will be a viable option in full-scale applications for treating mine impaired waters. In this respect, experimentation should be conducted with a continuous flow membrane system due to its widespread full-scale application. Testing of mine water samples from streams that are known to be more turbid than those tested in this study would allow for the identification of the optimal pretreatment stage prior to nanofiltration.

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Chapter 4 – BIOLOGICAL SULFATE REDUCTION

USE OF BIOLOGICAL SULFATE REDUCTION TO TREAT SULFATE IN SOUTHWESTERN VIRGINIA COAL MINE WATERS

Zachary E. Kemak², Gregory D. Boardman, Jeffrey Parks, Catherine Grey.

Abstract: Specific conductivity (SC) and total dissolved solids (TDS) have been identified as parameters of concern for waters originating from coal mine valley-fill structures. Batch reactors that utilized biological sulfate reduction were constructed in order to identify the optimal bioreactor mixture to encourage sulfate reduction, which would subsequently influence SC. Mixtures installed in each bioreactor were based on those found to provide optimal sulfate reduction in Cocos et al. (2002) and Neculita and Zagury (2008). Sulfate reduction occurred after approximately 20 days of operation. Sulfate levels declined from 30 to 40 percent depending on the bioreactor after 40 days of operation. Bioreactors were sampled in over a period 40 days in order to allow for acclimation of sulfate reducing bacteria. SC levels in excess of 13,000 $\mu\text{S}/\text{cm}$ were observed in all bioreactors tested after 40 days of operation. There were correlations greater than 0.90 for both bioreactors not containing manure/compost between SC and total alkalinity. Based on an analysis of the materials used in each bioreactor mixture, the manure/compost used in this study appeared to be the cause of the initial influx of SC in each of the bioreactors that incorporated the material. Further testing has been recommended in order to further optimize sulfate and SC reduction using biological sulfate reduction systems.

Additional Key Words: passive treatment, sulfate reducing bacteria, total dissolved solids, valley-fill.

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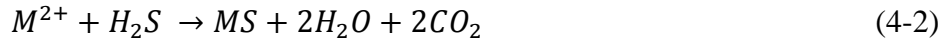
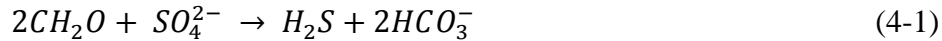
Introduction

Traditionally, specific conductivity (SC) and total dissolved solids (TDS) levels in mine effluent have not been a major concern for coal mining operations in the Eastern United States (US). With a rise in studies, which indicated that elevated SC and TDS in mining waters would negatively affect aquatic life (Cormier et al., 2011), the US Environmental Protection Agency (EPA) proposed a SC effluent limit of 500 $\mu\text{S}/\text{cm}$. Once a valley-fill structure has been installed by a coal mining operation, SC levels of streams emanating from these structures can remain elevated for several years after the installation of the system (Evans et al., 2014). Sulfate (SO_4^{2-}), which typically is the most common dissolved ion in mining impaired waters, has been found to have a negative effect on benthic macroinvertebrates in these waters (Timpano et al., 2010). The other dissolved ions of concern in coal mine waters include bicarbonate (HCO_3^-), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) (Orndorff et al., 2010).

Mining operations have historically utilized active treatment technologies that involve chemical addition to precipitate unwanted contaminants from the effluent emanating from coal valley-fill structures. In order to avoid the chemical and maintenance costs associated with active treatment technologies, mining operations are turning toward passive technologies as potential cost saving treatment options. Passive treatment decision making models have been developed to select passive treatment technologies based on the following water quality characteristics: pH, iron and aluminum, and dissolved oxygen (DO). SC and TDS are typically not incorporated into these decision-making models. These models suggest that biological sulfate reduction (BSR) should be used when waters are acidic and have DO, ferric iron, and aluminum levels above 1 mg/L (Skousen and Ziemkiewicz, 2005).

BSR utilizes an anaerobic environment to allow for the proliferation of sulfate reducing bacteria. In order to ensure anaerobic conditions, the oxidation-reduction potential (ORP) of the system is typically monitored. ORP levels below -100 mV have been identified as indicative of anaerobic conditions (Vasquez et al., 2016). Other parameters that can be examined to ensure ideal conditions for sulfate reducing bacteria are chemical oxygen demand (COD) and dissolved organic carbon (DOC). Hao et al. (1996) identified that COD/ SO_4^{2-} ranges of 0.7 to 1.5 were ideal for sulfate reducing

bacteria. Neculita and Zagury (2008) argued that DOC would provide a better indicator of the carbon available in the system since COD. Equations 4-1 and 4-2 below model the chemical reactions that occur in BSR systems:



The first phase of the reaction involves organic matter, modelled as CH₂O in Equation 1, reducing SO₄²⁻ to hydrogen sulfide gas (H₂S). If divalent metal cations are present in the system, modelled as M²⁺ in Equation 2, they will react with H₂S to precipitate a metal sulfide (MS).

There are several advantages in using BSR as compared to other passive treatment technologies. BSR is able handle influent water quality fluctuations well (Gusek, 2002). Other advantages offered by BSR include minimal maintenance and the ability to remove unwanted metals due to the aforementioned chemical reactions (Bowell, 2004). BSR can be designed in a variety of configurations, as batch or continuous flow systems, which allows for flexibility to best meet the needs of a mining operation (Kaksonen and Puhakka, 2007). There is also flexibility in terms of what materials are selected for each of the following components for the bioreactor mixture: nitrogen source, bacteria source, porous media, pH neutralizer, and carbon sources (Cocos et al., 2002). A combination of simple and complex organic carbon sources is used in these systems in order to provide both short-term and long-term carbon sources for the sulfate reducing bacteria in the system (Neculita et al., 2007). Common simple carbon sources include woodchips, sawdust, and hay; common complex organic carbon sources include manure and compost (Cocos et al., 2002; Neculita and Zagury, 2008; Hiibel et al., 2008; Vasquez et al., 2016).

There are also many disadvantages associated with operating a BSR system. Since these systems rely on bacteria, there may be a prolonged acclimation period until significant sulfate reduction is achieved (Rose, 2010); to bypass this issue, mining operations could obtain a seed from another operational BSR system to serve as an inoculum and speed up the start time of the bioreactors. If elevated levels of divalent metal cations are present in the system, there is a concern for plugging and clogging of the system with metal precipitates (Tsukamoto et al, 2004; Gusek, 2015). Bioreactors utilizing BSR have been found to decline in performance while operating at cold temperatures (Behum

et al., 2011; Gusek, 2002). Due to the high organic content of the bioreactor mixture, an increase of biochemical oxygen demand (BOD) in the effluent of bioreactors may need to be monitored (Gusek, 2015). The flexibility in terms of bioreactor configuration and mixture can be viewed in a negative light since there has not been an established criterion for successful implementation (Figueroa et al., 2007).

BSR has been shown to yield varying levels of success in reducing the SO_4^{2-} levels in mining waters (Behum et al., 2011; Cocos et al., 2002; de Vegt et al., 1998; Hiibel et al., 2008; Neculita and Zagury, 2008; Vasquez et al., 2016). SC monitoring was absent from each of these studies. Behum et al. (2011) examined an installed system at a coal mining operation and found there to be seasonal variations in terms of SO_4^{2-} reduction. A SO_4^{2-} reduction rate of 41 percent was achieved by the system examined in this study. Both Cocos et al. (2002) and Neculita and Zagury (2008) studied the use of multiple bioreactor mixtures in order to determine which mixture allowed for the highest overall ion reduction. The most successful reactors in each of these studies were able to achieve SO_4^{2-} reduction rates above 95 percent. Similar SO_4^{2-} reduction rates were achieved by the upflow anaerobic sludge blanket (UASB) configured BSR system built by de Vegt et al. (1998). The pilot BSR systems examined by Hiibel et al. (2008) had a SO_4^{2-} reduction rate of 63 percent and was found to be impacted by the competing presence of aerobic bacteria in the system. Vasquez et al. (2016) tested different mixtures for a continuous flow BSR system and was able to reach SO_4^{2-} reduction levels of 77 percent. This study observed a 30-day acclimation period for the sulfate reducing bacteria in each of the BSR systems tested.

The goal of this study was to test the feasibility of using BSR to reduce SO_4^{2-} levels in coal mine waters that are characteristic of southwestern Virginia. SC levels were also monitored. In order to evaluate each of the biological sulfate reducing bioreactors, the resulting SC value was compared to the proposed upper limit SC regulation of 500 $\mu\text{S}/\text{cm}$. Multiple reactor mixtures were tested in order to identify one mixture that showed promise for use in a treatment system. These mixtures were selected based on the work of Cocos et al. (2002) and Neculita and Zagury (2008). Ion concentrations were monitored to track the fate of ions in the reactor and their impact on SC.

Materials and Methods

Water samples were obtained from two, active, valley-fill sites at coal mines in southwestern Virginia that were known to have different levels of SC in receiving streams. The water samples coming from the Barton Hollow (BH) site were known to have moderate levels of SC due to an experimental design of the valley-fill structure designed to mitigate SC for the water exiting the structure. Experimental valley-fill structures are designed to incorporate materials that minimize SC and TDS release as well as limit the amount of water entering the structure. Upon exiting the valley-fill structure, the BH stream follows a rocky stream with well-defined banks that are densely vegetated and ultimately flows into a settling pond. Samples were collected from the BH site near the installed flume upstream of the aforementioned settling pond. The area surrounding the BH site had experienced a rainfall event, which may cause measured water characteristics to vary from average levels. The water samples coming from the Office Fill (OF) site were known to have high levels of SC since the valley-fill system in place utilizes a conventional design. Upon exiting the valley-fill structure at the OF site, the stream follows a rocky stream bed and crosses a gravel service road. Water samples were collected at the OF site at the point where the stream crossed the gravel service road and into a stream.

Due to its simplistic design, a batch reactor configuration was selected for experimentation. Using the recommended mixtures of Cocos et al. (2002) and Neculita and Zagury (2008), a set of mixtures were selected to be tested in the bioreactors. A summary of these mixtures can be seen in Table 4-1. The mixture STD was selected as the base mixture used, which was heavily influenced by the mixtures suggested in the aforementioned studies. The NS utilized the STD mixture minus sand. This was tested in order to see if the lack of a porous media would affect the performance of a batch reactor. The STDwFE mixture was STD mixture plus the addition of iron in the influent. Amid concerns that little to no sulfate reduction would occur due to the low levels of divalent metal cations, a solution with 40 mg/L of ferric sulfate was added to the influent of the STDwFE bioreactors. The NC bioreactors consisted of the STD mixture without manure/compost in order to determine whether or not the absence of a complex organic carbon source would impact the performance of the system.

Limestone, sand, manure/compost, and red oak mulch was obtained from a local landscape supplies business in Christiansburg, VA (USA). Sawdust was obtained from an on-campus woodshop that only worked with untreated lumber and wood products. Each material, with the exception of sawdust, was dried for three hours to measure the dry weight and calculate a moisture content to be used in determining the proper mixture distribution, as recommended by the literature. The materials were then weighed, thoroughly mixed together, and then placed into the bioreactors. The supernatant from anaerobic sludge from Peppers Ferry Wastewater Treatment Plant (WWTP) was used as the bacteria source for each of the reactors. Since supernatant from the anaerobic sludge was used as a bacteria source and not stream sediments as in the aforementioned studies, it was accounted for in the bioreactor mixture tabulation. The supernatant was added on a two percent basis to the influent water sample being added to each of the bioreactors. After each bioreactor was properly filled and sealed, all bioreactors were placed in a container containing a shallow layer of water to act as an additional seal for the bottom half of the columns. The container and the bioreactors were placed under a fume hood in case of hydrogen sulfide leaked from the bioreactors.

Table 4-1. Mixtures by percent dry weight for the standard (STD), no sand (NS), standard with iron (STDwFE), and no compost (NC) bioreactors.

Component	STD	NS	STDwFE	NC
Limestone	2	2	2	2
Urea	4	4	4	4
Sand	8	0	8	8
Manure/Compost	51	59	51	0
Sawdust	15	15	15	43
Red Oak Mulch	20	20	20	43

Once the mixtures and influent were implemented for each of the bioreactors, the reactors were allowed to operate at room temperature ($20.5^{\circ}\text{C} \pm 3^{\circ}\text{C}$). The bioreactors were manually mixed by inverting them one to two times each day. Each reactor was sampled in four to five day intervals for a 30-day period; an additional sample was collected on the 40th day of the study as well to allow for adequate acclimation of the sulfate reducing bacteria. During sampling, at least 50 mL of water sample was collected from each bioreactor; oxidation-reduction potential (ORP) was measured during sampling as a way

to ensure the bioreactors were anaerobic. Since the reactors were open to the atmosphere during sampling, nitrogen gas was applied to the bioreactor in order to purge any oxygen that might have entered the bioreactor.

The SC of all bioreactor samples were measured using an Omega CDH-SD1 conductivity meter. TDS was calculated from SC by using a SC to TDS ratio that was determined by measuring the TDS of samples with a known SC value. These SC ranges considered were as follows: 0-1,000 $\mu\text{S}/\text{cm}$, 1,000-2,000 $\mu\text{S}/\text{cm}$, and greater than 2,000 $\mu\text{S}/\text{cm}$. TDS testing was completed in accordance with Standard Methods 2540-C (Rice et al., 2012). Testing produced SC to TDS ratios of 0.64, 0.83, and 0.95 for the 0-1,000 $\mu\text{S}/\text{cm}$, 1,000-2,000 $\mu\text{S}/\text{cm}$, and greater than 2,000 $\mu\text{S}/\text{cm}$ ranges, respectively. ORP was measured using an ORPTestr 10meter (Oakton). Both inductively coupled plasma – mass spectrometry (ICP-MS) and anion ion chromatography (IC) were used to measure the cations and anions found in the samples collected. In order to ensure suspended solids were removed for ICP testing, all samples were filtered through Whatman glass fiber filters followed by 0.45 μm nylon filters. COD was measured using high-range Hach COD digester kits (HR+). TOC data were obtained using a TOC-V CSN TOC analyzer (Shimadzu). Alkalinity was measured via the titration methodology using 0.10 N sulfuric acid in accordance with Standard Methods 2320-B (Rice et al., 2012). The pH of the bioreactor samples was measured using an Oakton acorn series pH 6 meter. Turbidity was measured using a Orbeco-Hellige digital direct-reading turbidimeter. All meters used in this study were calibrated weekly.

The individual materials used in each of the bioreactor mixtures were then analyzed in order to better understand what each material contributed to the effluent. A predetermined mass of each material was placed in at least 100 mL of nanopure water and placed on shaker table for a 24-hour period. At least 50 mL of sample was taken from each of the test samples to be analyzed further using ICP-MS and the previously mentioned conductivity meter.

Results and Discussion

Initial water quality testing of the BH and OF mine waters yielded the results found in Table 4-2. As expected, the water emanating from the experimental valley-fill (BH) had

a lower average SC value than that coming from the conventional valley-fill (OF). Sulfate had the highest ionic presence in both mine waters tested. Iron and pH levels of both mine waters were below 1 mg/L and above 7.0, respectively, which signified that these mine waters would not be considered AMD.

Table 4-2. Average water quality characteristics of BH and OF water samples.

Characteristics	Barton Hollow (BH)	Office Fill (OF)
SC ($\mu\text{S}/\text{cm}$)	1,534	2,505
TDS (mg/L)	1,273	2,380
pH	7.53	7.62
Alkalinity (mg/L as CaCO_3)	100	198
Turbidity (NTU)	7.19	12.90
SO_4^{2-} (mg/L)	776	1,380
Cl^- (mg/L)	4.1	29.3
Ca^{2+} (mg/L)	181	346
Mg^{2+} (mg/L)	93.6	247
Na^+ (mg/L)	22.8	36.0
K^+ (mg/L)	7.7	10.5
Fe^{2+} (mg/L)	<1	<1

At least 50 mL of sample was collected from each bioreactor periodically over the 40 days of operation. Each of the bioreactors maintained ORP levels below the -100 mV threshold suggested by Vasquez et al. (2016) over the course of the 40 days of operation. The STD, NS, and STDwFE bioreactors averaged ORP levels at approximately -300 mV and the NC bioreactors averaged ORP levels at approximately -200 mV. Water samples collected from each of the bioreactors changed in color over the course of operation. The raw water influent samples had an average total suspended solid of 13 mg/L and 19 mg/L for the BH and OF water samples, respectively. Both raw water influent samples were clear in color prior to being added to the bioreactors. A noticeable shift in color of the water samples collected from each bioreactor was first observed after the first sampling event on the fourth day of operation. Water samples collected from the STD, NS, and STDwFE bioreactors were consistently dark brown in color over the course of the 40-day sampling period. Samples collected from these bioreactors ranged in terms of TSS between 1,640 mg/L and 22,620 mg/L. During the filtration process prior to preparing samples for ICP-MS, multiple Whatman glass fiber filters were used. A sludge-like layer developed on the surface of these filters after seconds of filtration. Water samples collected from the

NC bioreactors were light amber in color and had a noticeable number of solids in suspension. TSS values for samples collected from the NC bioreactors ranged from 1,500 mg/L to 3,500 mg/L.

After the 25th day of operation, the BH-NC bioreactor leaked and subsequently all water sample had drained from the system. The exact reason for the leak was not determined, but it was most likely due to not being properly sealed after the sampling event on the twenty-fifth day of operation. Due to this event, the BH-NC bioreactor was decommissioned and testing of this bioreactor had been terminated early. All data for this bioreactor up to that point has been included in the subsequent analysis.

Figure 4-1 displays how SC and SO_4^{2-} levels changed over the course of operation of the bioreactors. The reported SO_4^{2-} Figure 4-2 displays how total alkalinity and TOC levels changed over the 40-day operation period. The concentrations of the ions found in each of the observed samples were examined in an effort to explain the increase in SC levels. This presence of dissolved organics in the collected samples may have impacted the use of ICP-MS to collect data on the concentrations of dissolved ions present in the effluent samples. Since samples for ICP analysis required the addition of an acid, most samples produced humic acid after the sample was acidified. A discrepancy was observed when SO_4^{2-} concentrations obtained from anion IC were compared to those found by ICP-MS. For the samples collected on the fourth day of operation, the SO_4^{2-} ICP-MS data indicated reduction rates of approximately 30 to 40 percent occurred depending on the bioreactor examined. The anion IC data for the same sampling event had little discrepancy between the influent water samples in terms of SO_4^{2-} concentrations. Examination of the other major cations mentioned in Table 4-1 measured by ICP-MS indicated the divalent cations Ca^{2+} and Mg^{2+} also experienced significant reduction. Due to these drops in divalent ions, a corresponding drop in SC would have been expected. Humic acids have been found to act as an ion exchange mechanism in acidic environments which could possibly explain this occurrence during the ICP-MS testing (Pettit, 2004). This discrepancy led to utilization of anion IC for the measurement of SO_4^{2-} in the rest of the study. The growth/reduction rates from the first sampling event to the final sampling event for each of the remaining ions monitored by ICP-MS can be found in Figure 4-3.

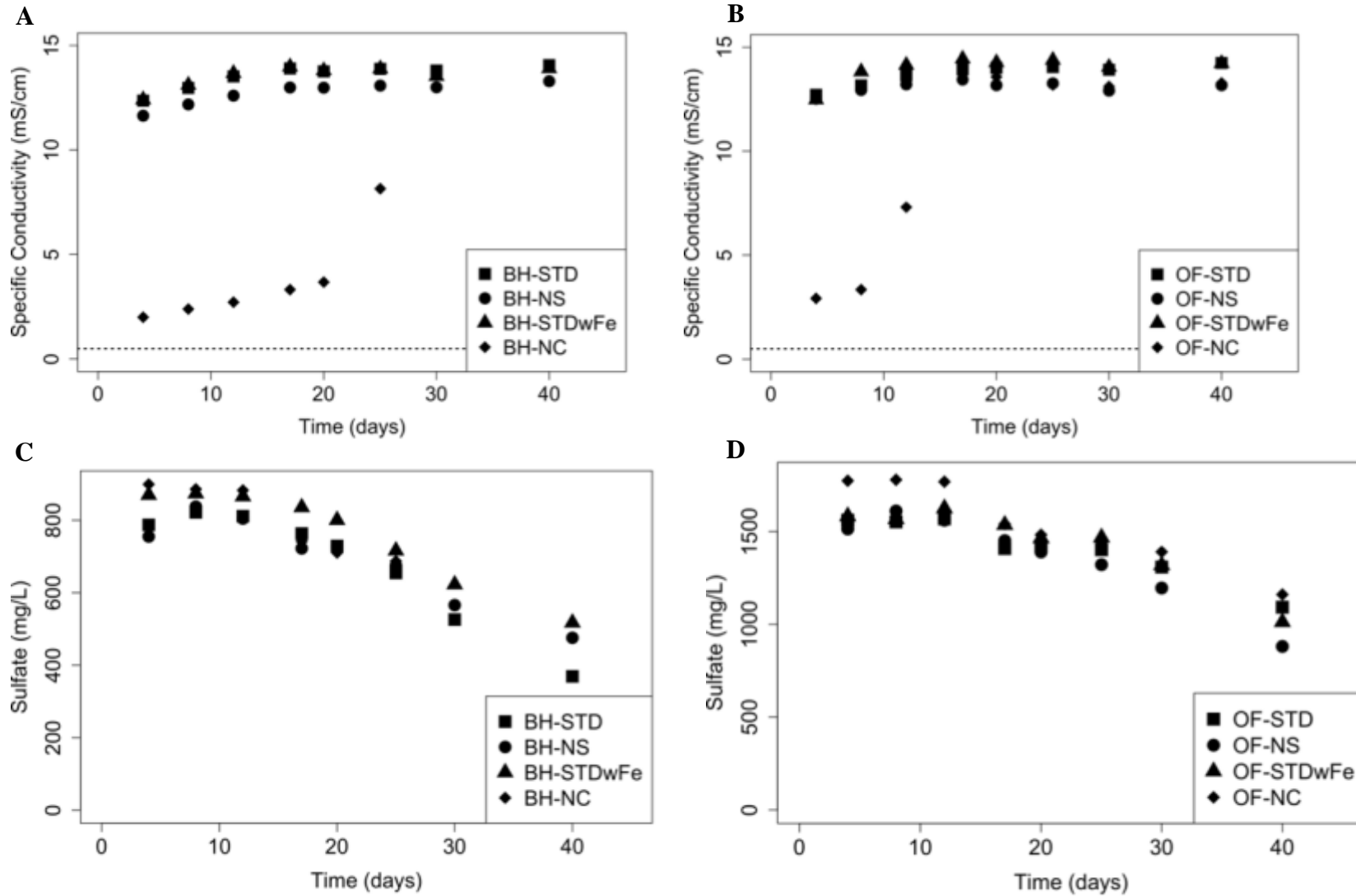


Figure 4-1. Observed SC values for BH (A) and OF (B) and observed SO_4^{2-} concentrations for BH (C) and OF (D).

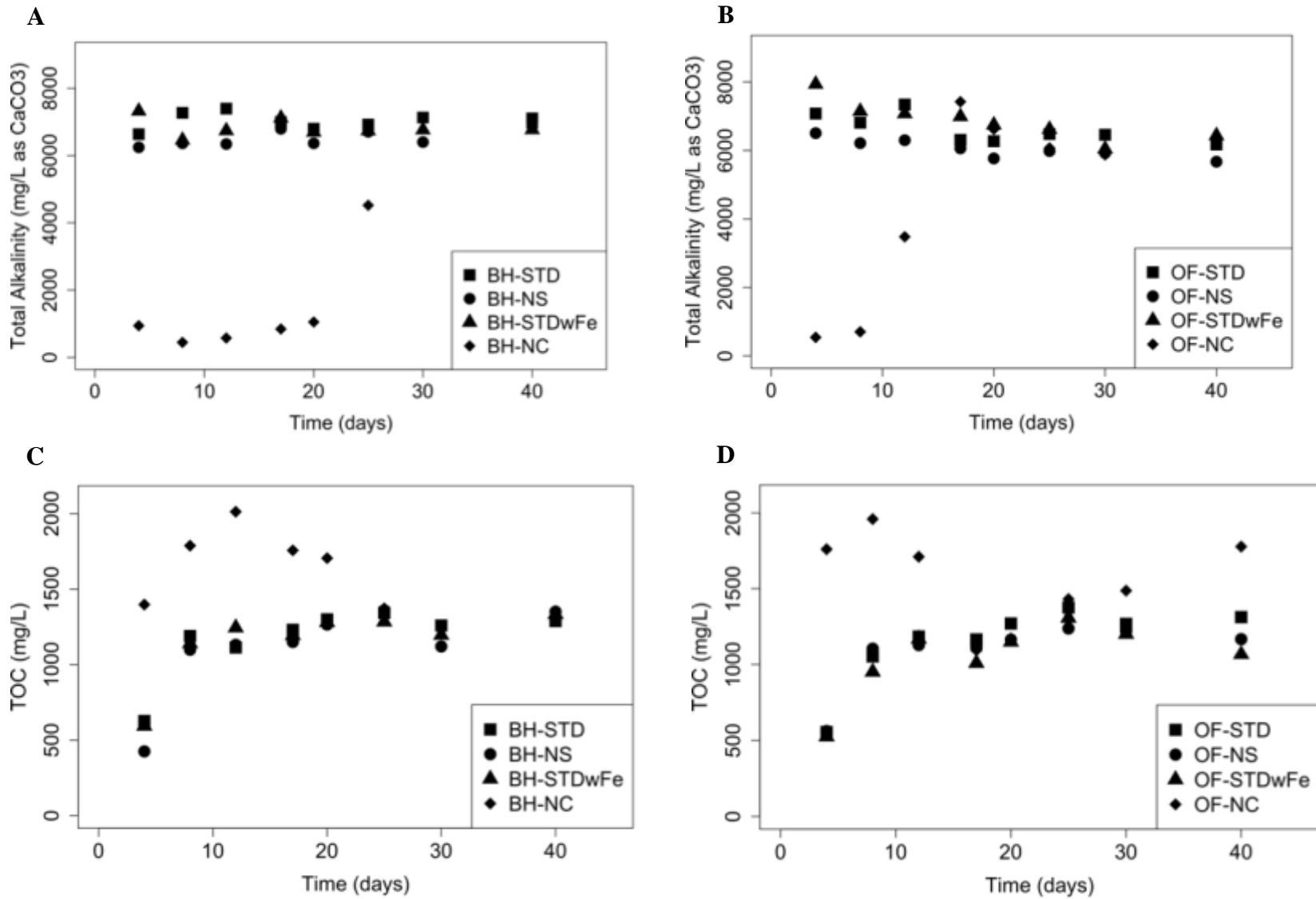


Figure 4-2. Observed total alkalinity for BH (A) and OF (B) samples and observed TOC for BH (C) and OF (D) samples

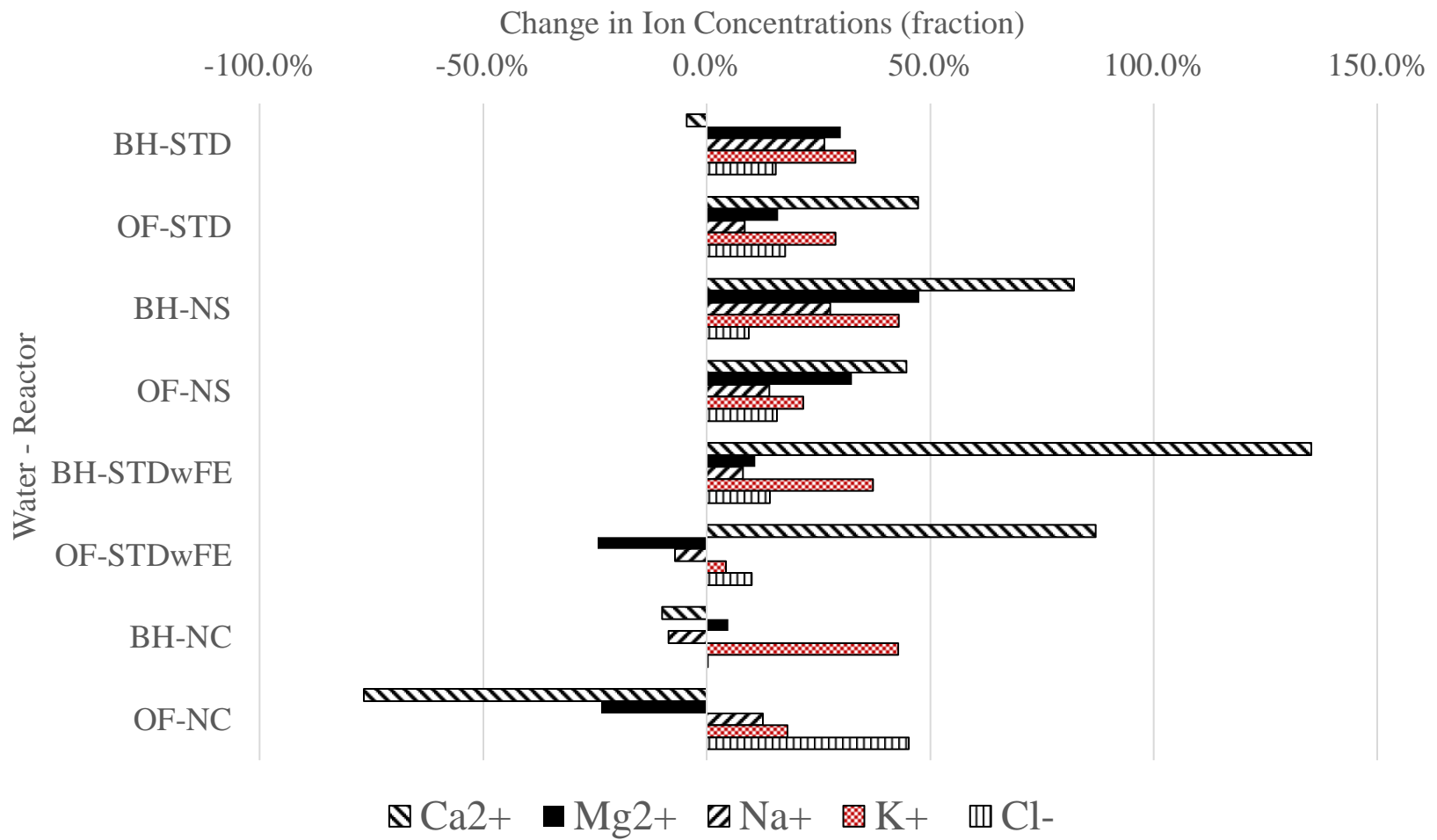


Figure 4-3. Ion growth/reduction rates from the first day of sampling (day 4) to the final day of sampling (day 40).

As evidenced by Figures 4-1 A and B, samples collected from all bioreactors maintained SC levels greater than the influent water samples for the duration of the sampling period. The STD, NS, and STDwFE bioreactors for each water sample tested had SC levels greater than 12,000 $\mu\text{S}/\text{cm}$ throughout the sampling period. The samples collected from the NC bioreactors progressively increased in SC until they reached levels comparable to the other bioreactors. The samples collected on the fortieth day of bioreactor operation all had an observed SC of greater than 13,000 $\mu\text{S}/\text{cm}$, which was two orders of magnitude greater than the proposed upper SC limit of 500 $\mu\text{S}/\text{cm}$ as set forth by Cormier et al. (2011).

Sulfate⁻ concentrations began to drop after approximately the twentieth day of operation. This acclimation period was comparable to that observed in the batch reactors operated by Cocos et al. (2002). By the fortieth day of operation, the BH bioreactors experienced SO_4^{2-} concentration reduction rates from the first sampling event of 53, 37, 41, and 24 percent for the STD, NS, STDwFE, and NC bioreactors, respectively. The OF bioreactors experienced SO_4^{2-} concentration reduction rates from the first sampling event of 30, 42, 36, and 35 percent for the STD, NS, STDwFE, and NC bioreactors, respectively. When compared to the SO_4^{2-} reduction rates observed by the most promising batch reactors from Cocos et al. (2002) and Neculita and Zagury (2008), the SO_4^{2-} reduction rates observed in this study were smaller by more than 50 percent. The SO_4^{2-} reduction rates observed in each of the bioreactors after forty days of operation were more comparable to those observed in the full-scale system of Behum et al. (2011).

Total alkalinity was one of the few parameters examined in this study that experienced significant increases along with SC. The final total alkalinity values obtained in this study were greater than the total alkalinity of 2,500 mg/L as CaCO_3 and 2,900 mg/L as CaCO_3 observed by Neculita and Zagury (2008) and Vasquez et al. (2016). This increase in total alkalinity was to be expected based on the generation of HCO_3^- during the sulfate reduction process as shown in Equation 4-1. The total alkalinity of the STD, NS, and STDwFE bioreactors all increased by a factor in excess of 6,000 percent for BH bioreactors and in excess of 3,000 percent for OF bioreactors on the fourth day of operation when compared to the influent water samples. The total alkalinity of the NC bioreactors

increased by a factor of approximately 840 percent for the BH bioreactor and 170 percent for the OF bioreactor on the fourth day of operation when compared to the influent water samples. Based on the trends observed in Figures 4-2 A and B, total alkalinity levels of the NC bioreactors reached similar levels of the other bioreactors after approximately 17 days of operation of the OF-NC bioreactor; it is unclear at what point the BH-NC bioreactor reached similar total alkalinity levels due its early decommissioning. Of the bioreactors tested, only the NC bioreactors produced a coefficient of correlation greater than 0.90 between total alkalinity and SC; the coefficient of correlation for BH-NC was 0.97 and the coefficient of correlation for OF-NC was 0.99. This correlation would indicate that greater than 90 percent of the variation in SC is explained by total alkalinity in NC bioreactors. Coefficients of correlation between total alkalinity and SC for the other bioreactors studied were all below 0.80.

Examination of the ion growth/reduction rates from the first sampling event to the final sampling event shows that most of the ions examined increased over time (Figure 4-3). Ca^{2+} experienced the highest growth in all but three of the bioreactors studied (BH-STD, BH-NC, OF-NC). Both K^{+} and Cl^{-} consistently increased over time in all bioreactor mixtures tested. The NC bioreactors for each of the mine waters tested had no ionic growth rates above 50 percent, and had net reduction occur for at least two ions.

The individual materials used in each of the bioreactor mixtures were then analyzed in order to better understand what each material contributed to the effluent. The results of this testing (Table 4-3) indicated that the manure/compost used in this study as the primary contributor of SC to the effluent with a contribution level of nearly 80 ($\mu\text{S}/\text{cm}$)/g, which was greater than four times the next highest SC contributor in red oak mulch. The compost/manure was also found to contribute the most total alkalinity to the effluent. Compost/manure's total alkalinity contribution was found to be greater than that of the designated pH neutralizer, limestone. Given its total alkalinity contribution, the compost/manure used in this study could negate the need for limestone in the system. Examination of the ions tested shows the compost/manure to be the highest contributor to each of the ions tested except for Mg^{2+} in which the limestone is the highest contributor.

Table 4-3. Characteristics of materials used in bioreactors.

Material	SC ((μ S/cm)/g)	Alkalinity ((mg CaCO ₃)/g)	SO ₄ ²⁻ (mg/g)	Ca ²⁺ (mg/g)	Mg ²⁺ (mg/g)	Na ⁺ (mg/ g)	K ⁺ (mg/g)
Limestone	8.42	3.04	0.03	0.04	0.07	0.00	0.01
Sand	0.84	0.12	-0.01	0.01	0.00	0.00	0.00
Sawdust	11.21	0.44	0.02	0.10	0.05	0.02	0.36
Compost	79.95	3.94	0.07	0.11	0.06	0.23	1.71
Red Oak Mulch	16.81	0.50	0.00	0.06	0.02	0.01	0.64

Another noticeable change among the samples was an increase in pH. The samples collected from the BH bioreactors had an average pH of 8.58 on the final day of sampling. The samples collected from OF bioreactors had an average pH of 8.50 on the final day of sampling. Correlation analysis between observed pH and total alkalinity for BH bioreactors indicated that only the NC bioreactor yielded a coefficient of correlation greater than 0.90. Correlation analysis between observed pH and total alkalinity for the OF bioreactors indicated that the NS, STDwFE, and NC bioreactors had coefficients of correlation greater than 0.90.

Conclusions

The SC measured in each of the BSR bioreactors at the end of 40 days of operation were all well in excess of the proposed upper limit of 500 μ S/cm. Sulfate reduction appeared to occur after 20 days of operation in each of the bioreactors. Despite achieving an average of 37 percent SO₄²⁻ reduction after 40 days of operation, SC levels in all bioreactor samples were above 13,000 μ S/cm on the final day of sampling. The manure/compost utilized in this study was identified as the probable cause for the increase in SC based on material analysis testing. Daily testing, especially in the early stages of operations, would have allowed for better clarity of potential trends in data.

There are still many avenues that can be explored in terms of SC reduction in biological sulfate reduction reactor systems. For similar batch reactor studies, long-term monitoring of SC levels would help provide a better understanding of SC trends and identifying potential SC contributors. Daily sampling of batch reactors would allow for better monitoring of trends in water quality changes. SC monitoring of full-scale BSR

bioreactor installations would also help in this endeavor and environmental conditions could be monitored as well to see if there are any correlations between SC reduction/increase due to temperature changes.

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Chapter 5 – CONCLUSIONS

Nanofiltration proved to be a potential option to mitigate specific conductivity (SC) and total dissolved solids (TDS) levels of mine waters. The DK and NFX nanofilters provided SC reduction rates in excess of 80 percent for both mine water samples tested. The testing conducted using the NF270 nanofilter yielded variable levels of SC reduction and it was unable to reduce SC levels of the water with high SC content to the proposed limit. The results indicated that as ion concentrations increased in the higher SC mine water tested, performance in terms of SC reduction declined. Testing that incorporated microfiltration and simulated-sand filtration as pretreatment prior to nanofiltration did not indicate that SC performance would improve for the water samples tested. Future testing on mine waters that have higher turbidity than those tested in this study should be used to identify optimal pretreatment options for nanofiltration.

Biological sulfate reduction systems proved to be ineffective in terms of the reduction of SC. Sulfate reduction was identified to occur after approximately 20 days of operation in each of the bioreactors monitored when sulfate levels fell below the value collected on the first sampling event. After 40 days of operation, all samples collected had SC levels in excess of 13,000 $\mu\text{S}/\text{cm}$. Additional material analysis indicated that the manure/compost contributed the most SC to the effluent. Further testing will be required to gain a better understanding of the increase of SC in biological sulfate reduction systems and identify optimal materials for biological sulfate reduction systems.

Appendix A: Characterization of Mine Waters

Table A-1. Barton Hollow water quality parameters.

SAMPLE	SAMPLEID	SC $\mu\text{S/cm}$	TDS (meter)	TDS (test)	TSS	pH	ALKALINITY	HARDNESS	TURBIDITY NTU
			mg/L	mg/L	mg/L		mg/L as CaCO ₃	mg/L as CaCO ₃	
BH	BH1	1539	1030	1277	8	7.72	100	839.9	4.95
BH	BH2	1533	1013	1272	18	7.51	100	840.6	10.5
BH	BH3	1530	1023	1270	9	7.45	99	832.4	5.25
BH	BH4	1532	1014	1272	16	7.44	99	835.2	8.07
BH	BH AVG	1534	1020	1272.805	13	7.53	100	837.0	7.19

SAMPLE	SAMPLEID	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
		mg/L	mg/L	mg/L	mg/L	mg/L
BH	BH1	773.2	182.9	93.3	22.5	7.7
BH	BH2	779.2	182.3	93.9	23.0	7.7
BH	BH3	776.6	180.1	93.2	22.8	7.6
BH	BH4	774.2	180.1	93.9	23.0	7.8
BH	BH AVG	775.8	181.4	93.6	22.8	7.7

Table A-2. Office Fill water quality parameters.

SAMPLE	SAMPLEID	SC μS/cm	TDS (meter) mg/L	TDS (test) mg/L	TSS mg/L	pH	ALKALINITY mg/L as CaCO3	HARDNESS mg/L as CaCO3	TURBIDITY NTU
OF	OF1	2500	1670	2375	36	7.64	216	1893.1	24.5
OF	OF2	2500	1670	2375	21	7.59	181	1866.1	12.5
OF	OF3	2510	1670	2385	5	7.62	222	1862.6	4.7
OF	OF4	2510	1670	2385	12	7.61	173	1889.5	9.89
OF	OFAVG	2505	1670	2379.75	19	7.62	198	1877.8	12.90

SAMPLE	SAMPLEID	SO ₄ ²⁻ mg/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Na ⁺ mg/L	K ⁺ mg/L
OF	OF1	1,352.0	348.4	249.3	36.3	11.1
OF	OF2	1,386.0	343.5	245.7	35.8	10.3
OF	OF3	1,403.0	342.1	245.7	35.8	10.3
OF	OF4	1,386.0	349.9	247.5	36.1	10.5
OF	OFAVG	1381.8	346.0	247.1	36.0	10.5

Appendix B: Chapter 3 Supporting Data and Information

Table B-1. Barton Hollow NF270 nanofiltration effluent characteristics.

SAMPLE	SAMPLEID	ID	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)		
BH	BH1	1	NF270	1	8.0	116.0		
BH	BH1	2	NF270	1	8.0	116.0		
BH	BH1	3	NF270	1	8.0	116.0		
BH	BH1	EXT1	NF270	6	8	116.03		
BH	BH1	EXT2	NF270	6	8	116.03		
BH	BH2	EXT3	NF270	7	8	116.03		
BH	BH2	EXT4	NF270	7	8	116.03		

SAMPLEID	ID	SC (μS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
BH1	1	339	226	231	7.77	81	131.1	0.71
BH1	2	324	217	220	7.95	80	123.5	0.59
BH1	3	351	233	239	7.92	86	137.1	0.53
BH1	EXT1	519	346	353	7.82	59	216.4	0.51
BH1	EXT2	507	338	345	7.99	70	203.7	0.42
BH2	EXT3	543	361	369	7.86	86	219.3	0.42
BH2	EXT4	757	505	515	8.01	90	327.5	0.46
AVERAGE		477.14	318.00	324.46	7.90	78.81	194.10	0.52
STDEV		154.78	103.19	105.25	0.09	10.83	72.14	0.10

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
BH1	1	54.9	26.2	16.0	14.3	4.1
BH1	2	48.5	23.5	15.8	14.2	4.0
BH1	3	58.1	25.2	18.1	14.5	4.2
BH1	EXT1	163.7	41.5	27.5	13.7	4.1
BH1	EXT2	141.3	38.0	26.5	14.1	4.1
BH2	EXT3	143.6	41.9	27.9	14.2	4.1
BH2	EXT4	245.4	61.5	42.4	15.7	4.7
	AVERAGE	122.21	36.82	24.89	14.39	4.20
	STDEV	72.79	13.44	9.42	0.64	0.22

Table B-2. Barton Hollow DK nanofiltration effluent characteristics.

SAMPLE	SAMPLEID	ID	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
BH	BH2	5	DK	1	8.0	116.0
BH	BH2	6	DK	1	8.0	116.0
BH	BH2	7	DK	1	8.0	116.0

SAMPLEID	ID	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
BH2	5	221	148	150	7.63	48	48.5	0.56
BH2	6	310	206	211	7.67	65	94.3	0.64
BH2	7	281	187	191	7.6	58	93.7	0.54
	AVERAGE	270.67	180.33	184.05	7.63	56.87	78.80	0.58
	STDEV	45.39	29.57	30.87	0.04	8.87	26.25	0.05

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
BH2	5	21.0	10.5	5.4	17.5	13.3
BH2	6	53.4	14.6	14.1	20.5	6.1
BH2	7	53.9	15.8	13.2	20.1	6.0
	AVERAGE	42.76	13.62	10.92	19.35	8.46
	STDEV	18.83	2.81	4.76	1.61	4.20

Table B-3. Barton Hollow NFX nanofiltration effluent characteristics.

SAMPLE	SAMPLEID	ID	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
BH	BH1	9	NFX	1	8.0	116.0
BH	BH1	10	NFX	1	8.0	116.0
BH	BH1	11	NFX	1	8.0	116.0

SAMPLEID	ID	SC (μS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
BH1	9	197.1	131.1	134	7.62	63	58.7	0.51
BH1	10	203	135	138	8.02	64	59.8	0.5
BH1	11	248	165	169	7.83	67	78.7	0.5
AVERAGE		216.03	143.70	146.90	7.82	64.92	65.73	0.50
STDEV		27.84	18.55	18.93	0.20	2.18	11.28	0.01

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
BH1	9	6.8	15.7	4.7	15.7	4.9
BH1	10	8.0	15.9	4.9	15.3	4.7
BH1	11	23.5	19.4	7.4	16.5	5.1
AVERAGE		12.76	17.00	5.67	15.82	4.90
STDEV		9.30	2.07	1.49	0.57	0.17

Table B-4. Office Fill NF270 nanofiltration effluent characteristics.

SAMPLE	SAMPLEID	ID	TEST	TYPE	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
OF	OF1	OF1	NF	NF	NF270	4	8.0	116.03
OF	OF1	OF2	NF	NF	NF270	4	8.0	116.03
OF	OF1	OF3	NF	NF	NF270	4	8.0	116.03
OF	OF2	EXTOF1	NF	NF	NF270	6	8	116.03
OF	OF2	EXTOF2	NF	NF	NF270	6	8	116.03
OF	OF4	EXTOF3	NF	NF	NF270	8	8	116.03
OF	OF4	EXTOF4	NF	NF	NF270	8	8	116.03

SAMPLEID	ID	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
OF1	OF1	1165	776	967	8.13	195	565.2	0.61
OF1	OF2	1245	828	1033	8.12	203	603.0	0.56
OF1	OF3	1424	949	1182	8.14	201	717.4	0.53
OF2	EXTOF1	806	537	548	8.15	171	367.3	0.48
OF2	EXTOF2	849	566	577	8.15	191	384.8	0.52
OF4	EXTOF3	811	540	551	8.14	208	353.8	0.47
OF4	EXTOF4	915	609	622	8.17	209	411.0	0.49
	AVERAGE	1030.71	686.43	783.04	8.14	196.64	486.06	0.52
	STDEV	246.24	163.95	268.51	0.02	13.17	141.98	0.05

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
OF1	OF1	374.4	95.7	79.5	23.0	6.2
OF1	OF2	415.4	92.6	90.6	23.9	6.7
OF1	OF3	545.2	104.1	111.5	24.8	7.0
OF2	EXTOF1	245.4	64.8	50.1	19.7	5.3
OF2	EXTOF2	177.5	67.2	52.9	19.6	5.1
OF4	EXTOF3	186.4	59.6	49.9	19.5	5.1
OF4	EXTOF4	235.6	59.0	64.3	21.0	5.5
	AVERAGE	311.41	77.58	71.25	21.63	5.83
	STDEV	137.30	19.13	23.64	2.21	0.80

Table B-5. Office Fill DK nanofiltration effluent characteristics.

SAMPLE	SAMPLEID	ID	TEST	TYPE	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
OF	OF1	OF4	NF	NF	DK	2	8	116.03
OF	OF1	OF5	NF	NF	DK	2	8	116.03
OF	OF1	OF6	NF	NF	DK	2	8	116.03

SAMPLEID	ID	SC (μS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
OF1	OF4	284	189	193	7.8	83	65.4	0.52
OF1	OF5	420	280	286	7.92	105	121.7	0.44
OF1	OF6	414	276	282	7.74	88	126.2	0.56
	AVERAGE	372.67	248.33	253.41	7.82	91.93	104.40	0.51
	STDEV	76.85	51.42	52.26	0.09	11.59	33.89	0.06

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
OF1	OF4	21.9	12.3	8.4	25.5	7.1
OF1	OF5	57.3	13.8	21.3	26.8	7.5
OF1	OF6	71.4	13.6	22.5	24.3	6.6
	AVERAGE	50.21	13.25	17.39	25.52	7.07
	STDEV	25.54	0.80	7.79	1.29	0.43

Table B-6. Office Fill NFX nanofiltration effluent characteristics.

SAMPLE	SAMPLEID	ID	TEST	TYPE	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
OF	OF2	OF7	NF	NF	NFX	2	8	116.03
OF	OF2	OF8	NF	NF	NFX	2	8	116.03
OF	OF2	OF9	NF	NF	NFX	2	8	116.03
OF	OF1	EXTOF5	NF	NF	NFX	7	8	116.03
OF	OF1	EXTOF6	NF	NF	NFX	7	8	116.03

SAMPLEID	ID	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
OF2	OF7	274	182	186	7.91	84	61.8	0.47
OF2	OF8	302	201	205	7.87	81	75.1	0.42
OF2	OF9	318	211	216	7.83	81	80.8	0.43
OF1	EXTOF5	698	465	475	7.83	109	271.1	0.64
OF1	EXTOF6	513	342	349	7.85	97	174.1	0.52
	AVERAGE	421.00	280.20	286.28	7.86	90.56	132.59	0.50
	STDEV	181.36	121.11	123.33	0.03	12.40	89.33	0.09

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
OF2	OF7	20.1	14.4	6.3	25.3	6.9
OF2	OF8	33.9	15.2	9.0	24.5	6.5
OF2	OF9	40.1	16.4	9.7	24.3	6.4
OF1	EXTOF5	192.1	50.7	35.2	24.4	6.6
OF1	EXTOF6	105.1	33.6	22.0	23.8	6.4
	AVERAGE	78.26	26.08	16.44	24.47	6.59
	STDEV	71.57	15.91	12.10	0.55	0.19

Table B-7. Barton Hollow effluent characteristics after microfiltration and nanofiltration.

SAMPLE	SAMPLEID	ID	TEST	TYPE	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
BH	BH2 (TM10- P2)	BHMF1	MFNF	NF	NFX	3	8	116.03
BH	BH2 (TM10- P2)	BHMF2	MFNF	NF	NFX	3	8	116.03
BH	BH2 (TM10- P2)	BHMF3	MFNF	NF	NFX	3	8	116.03

SAMPLEID	ID	SC (μS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
BH2 (TM10- P2)	BHMF1	265	176	180	7.78	59	82.6	0.64
BH2 (TM10- P2)	BHMF2	313	208	213	7.86	62	99.3	0.46
BH2 (TM10- P2)	BHMF3	341	227	232	7.83	65	107.8	0.46
	AVERAGE	306.33	203.67	208.31	7.82	62.21	96.57	0.52
	STDEV	38.44	25.77	26.14	0.04	3.35	12.81	0.10

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
BH2 (TM10-P2)	BHMF1	39.2	18.7	8.8	13.4	4.0
BH2 (TM10-P2)	BHMF2	56.1	21.7	11.0	14.7	4.4
BH2 (TM10-P2)	BHMF3	63.7	23.5	12.0	15.3	4.6
	AVERAGE	52.99	21.27	10.58	14.48	4.36
	STDEV	12.57	2.44	1.64	0.98	0.30

Table B-8. Barton Hollow effluent characteristics after simulated-sand filtration and nanofiltration.

SAMPLE	SAMPLEID	ID	TEST	TYPE	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
BH	BH2 (GF/B)	BHSF1	SFNF	NF	NFX	4	8	116.03
BH	BH2 (GF/B)	BHSF2	SFNF	NF	NFX	4	8	116.03
BH	BH2 (GF/B)	BHSF3	SFNF	NF	NFX	4	8	116.03

SAMPLEID	ID	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
BH2 (GF/B)	BHSF1	188.7	125.8	128	7.79	54	45.1	0.5
BH2 (GF/B)	BHSF2	209	139	142	7.83	57	50.5	0.53
BH2 (GF/B)	BHSF3	223	149	152	7.73	57	57.8	0.48
	AVERAGE	206.90	137.93	140.69	7.78	56.18	51.13	0.50
	STDEV	17.25	11.64	11.73	0.05	1.65	6.40	0.03

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
BH2 (GF/B)	BHSF1	12.8	11.4	4.1	14.5	4.4
BH2 (GF/B)	BHSF2	17.3	12.0	5.0	15.9	4.8
BH2 (GF/B)	BHSF3	23.7	12.6	6.5	15.5	4.7
	AVERAGE	17.92	11.96	5.18	15.30	4.64
	STDEV	5.48	0.60	1.20	0.75	0.20

Table B-9. Office Fill effluent characteristics after microfiltration and nanofiltration.

SAMPLE	SAMPLEID	ID	TEST	TYPE	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
OF	OF4 (TM10- P1)	OFMF1	MFNF	NF	NFX	6	8	116.03
OF	OF4 (TM10- P1)	OFMF2	MFNF	NF	NFX	6	8	116.03
OF	OF4 (TM10- P1)	OFMF3	MFNF	NF	NFX	6	8	116.03

SAMPLEID	ID	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
OF4 (TM10- P1)	OFMF1	517	344	352	7.93	93	167.4	0.47
OF4 (TM10- P1)	OFMF2	530	353	360	7.98	103	181.6	0.45
OF4 (TM10- P1)	OFMF3	639	425	435	7.99	97	238.4	0.45
	AVERAGE	562.00	374.00	382.16	7.97	97.72	195.81	0.46
	STDEV	67.00	44.40	45.56	0.03	4.83	37.54	0.01

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
OF4 (TM10- P1)	OFMF1	107.7	31.2	21.8	23.6	6.5
OF4 (TM10- P1)	OFMF2	102.7	27.8	27.4	24.2	6.6
OF4 (TM10- P1)	OFMF3	162.2	27.8	41.2	22.6	6.1
	AVERAGE	124.20	28.89	30.14	23.46	6.40
	STDEV	33.00	1.97	9.99	0.80	0.22

Table B-10. Office Fill effluent characteristics after simulated-sand filtration and nanofiltration.

SAMPLE	SAMPLEID	ID	TEST	TYPE	FILTER	FILTER #	PRESSURE (bar)	PRESSURE (psi)
OF	OF3 (GF/B)	OFSF1	SFNF	NF	NFX	5	8	116.03
OF	OF3 (GF/B)	OFSF2	SFNF	NF	NFX	5	8	116.03
OF	OF3 (GF/B)	OFSF3	SFNF	NF	NFX	5	8	116.03

SAMPLEID	ID	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	pH	ALKALINITY (mg/L as CaCO3)	HARDNESS (mg/L as CaCO3)	TURBIDITY (NTU)
OF3 (GF/B)	OFSF1	572	382	389	8.02	112	199.6	0.55
OF3 (GF/B)	OFSF2	495	330	337	8.04	114	164.7	0.46
OF3 (GF/B)	OFSF3	602	401	409	8.04	112	219.8	0.49
	AVERAGE	556.33	371.00	378.31	8.03	112.38	194.68	0.50
	STDEV	55.19	36.76	37.53	0.01	1.22	27.89	0.05

SAMPLEID	ID	SO₄²⁻ (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)
OF3 (GF/B)	OFSF1	121.7	38.4	25.2	23.5	6.4
OF3 (GF/B)	OFSF2	81.3	30.5	21.6	22.9	6.2
OF3 (GF/B)	OFSF3	131.9	30.5	35.0	22.7	6.1
	AVERAGE	111.64	33.13	27.28	23.03	6.24
	STDEV	26.75	4.59	6.95	0.41	0.15

R Code to Conduct Multiple Comparison Statistical Analysis

```
rm(list = ls(all=TRUE))
library(foreign)
library(agricolae)
library(lattice)
library(readxl)

#read in excel data file
xall <- read_excel("ExperimentationRtest.xlsx",sheet="BHMembraneTestingDataFINAL")
names(xall)

#remove unwanted datasets from consideration
x <- xall[xall$FILTER != "TM10",]
x <- x[x$FILTER != "XT",]
x <- x[!is.na(x$SC),]
tapply(x$SC, list(x$SAMPLE, x$FILTER), mean, na.rm=TRUE)
x$TID = as.factor(x$TID)

#apply summary statistics and tukey multiple comparison test
tx <- with(x, interaction(TID, TEST))
anovaSC <- aov(x$SC~tx)
summary(anovaSC)
HSD.test(anovaSC, "tx", group=TRUE, console=TRUE)
```

Results of Multiple Comparison Statistical Analysis

R Output for BH Nanofiltration Only Testing

HSD Test for x\$SC

Mean Square Error: 14941.97

tx, means

	x.SC	std r	Min	Max
1.NF	477.1429	154.78418	7	324.0 757
2.NF	270.6667	45.39089	3	221.0 310
3.NF	216.0333	27.84068	3	197.1 248

alpha: 0.05 ; Df Error: 10

Critical Value of Studentized Range: 3.876777

Harmonic Mean of Cell Sizes 3.705882

Honestly Significant Difference: 246.1665

Means with the same letter are not significantly different.

Groups, Treatments and means

a	1.NF	477.1
ab	2.NF	270.7
b	3.NF	216

Results of Multiple Comparison Statistical Analysis (continued)

R Output for OF Nanofiltration Only Testing

HSD Test for x\$SC

Mean Square Error: 42265.67

tx, means

	x.SC	std	r	Min	Max
6.NF	1030.7143	246.24020	7	806	1424
7.NF	372.6667	76.84617	3	284	420
8.NF	421.0000	181.36427	5	274	698

alpha: 0.05 ; Df Error: 12

Critical Value of Studentized Range: 3.772929

Harmonic Mean of Cell Sizes 4.43662

Honestly Significant Difference: 368.2531

Means with the same letter are not significantly different.

Groups, Treatments and means

a	6.NF	1031
b	8.NF	421
b	7.NF	372.7

Results of Multiple Comparison Statistical Analysis (continued)

R Output for BH Nanofiltration with Pretreatment Testing

HSD Test for x\$SC

Mean Square Error: 849.9556

tx, means

	x.SC	std r	Min	Max
1.MFNF	306.3333	38.43609	3 265.0	341
1.NFX	216.0333	27.84068	3 197.1	248
3.SFNF	206.9000	17.24616	3 188.7	223

alpha: 0.05 ; Df Error: 6

Critical Value of Studentized Range: 4.339195

Honestly Significant Difference: 73.03763

Means with the same letter are not significantly different.

Groups, Treatments and means

a	1.MFNF	306.3
b	1.NFX	216
b	3.SFNF	206.9

Results of Multiple Comparison Statistical Analysis (continued)

R Output for OF Nanofiltration with Pretreatment Testing

HSD Test for x\$SC

Mean Square Error: 18330.33

tx, means

	x.SC	std r	Min	Max
2.MFNF	562.0000	67.0000	3 517	639
4.SFNF	556.3333	55.1936	3 495	602
8.NFX	421.0000	181.3643	5 274	698

alpha: 0.05 ; Df Error: 8

Critical Value of Studentized Range: 4.041036

Harmonic Mean of Cell Sizes 3.461538

Honestly Significant Difference: 294.065

Means with the same letter are not significantly different.

Groups, Treatments and means

a	2.MFNF	562
a	4.SFNF	556.3
a	8.NFX	421

Table B-11. ICP-MS results from membrane residuals taken from NF270 nanofilter.

ID	DRY SOLIDS WT (mg)	SO42- (mg/L)	Ca2+ (mg/L)	Mg2+ (mg/L)	Na+ (mg/L)	K+ (mg/L)
S1	0.90	42.40	14.07	2.11	0.49	0.26
S2	3.25	196.95	55.92	12.47	1.38	0.60
S3	2.30	73.43	24.46	2.88	0.37	0.19
AVG	2.15	104.26	31.48	5.82	0.75	0.35

Appendix C: Chapter 4 Supporting Data and Information

Table C-1. BH-STD bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
BH-STD	A1	10/25/16	4	22.8	12360	8220	11742	N/A	8.93	6633.59
BH-STD	A2	10/29/16	8	24.9	12970	8640	12322	N/A	9.01	7269.4
BH-STD	A3	11/2/16	12	21.4	13520	9000	12844	N/A	8.97	7394.96
BH-STD	A4	11/7/16	17	19.7	13900	9250	13205	5920	8.82	7001.27
BH-STD	A5	11/10/16	20	19.2	13760	9170	13072	9948	8.75	6799.1
BH-STD	A6	11/15/16	25	21.2	13880	9240	13186	8000	8.65	6923.24
BH-STD	A7	11/20/16	30	18.9	13800	9210	13110	1720	8.68	7128.95
BH-STD	A8	11/30/16	40	23	14060	9380	13357	10580	8.6	7105.22

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO ₄ ²⁻ ICP (mg/L)	SO ₄ ²⁻ IC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	NH ₃ -N (mg/L)
A1	N/A	2660	626.4	528.6	787.1	32.6	36.4	39.0	260.6	62.9	16.88	N/A
A2	N/A	6300	1188.8	493.8	821.6	18.3	25.1	36.9	248.7	63.1	21.64	0.411
A3	-362	6640	1113	605.7	810.9	19.88	31.36	41.73	297.1	70.3	21.80	0.482
A4	-219	10030	1230	655.5	763.2	24.26	38	44.96	329.5	66.8	13.5	0.431
A5	-310	5160	1299.2	666	728.9	24.21	39.73	47.88	344.2	69.8	15.8	3.29
A6	-305	5550	1342.6	609.6	654.6	24.17	39.75	47.06	343.8	65.7	16.8	4.46
A7	-307	10115	1258.8	508.6	526.0	26.85	41.09	46.54	331.7	56.5	4.4	14.15
A8	-314	11685	1288.2	324.5	369.0	31.15	47.32	49.32	347.5	72.6	4.0	20.6

Table C-2. BH-NS bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
BH-NS	B1	10/25/16	4	22.8	11640	7760	11058	N/A	9.02	6244.29
BH-NS	B2	10/29/16	8	24.5	12180	8120	11571	N/A	8.98	6362.86
BH-NS	B3	11/2/16	12	21.3	12600	8400	11970	N/A	8.91	6341.58
BH-NS	B4	11/7/16	17	19.6	12990	8660	12341	5000	8.82	6792.01
BH-NS	B5	11/10/16	20	19	12980	8650	12331	4720	8.73	6362.86
BH-NS	B6	11/15/16	25	21.4	13080	8720	12426	2960	8.67	6703.34
BH-NS	B7	11/20/16	30	18.7	13000	8710	12350	3440	8.66	6399.34
BH-NS	B8	11/30/16	40	23	13290	8870	12626	11200	8.61	6862.95

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO ₄ ²⁻ ICP (mg/L)	SO ₄ ²⁻ IC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	NH ₃ -N (mg/L)
B1	N/A	1980	425.0	457.2	754.9	15.8	27.3	35.2	230.9	60.2	18.51	N/A
B2	N/A	4300	1098.2	509.9	837.4	20.3	25.8	37.2	251.8	65.6	19.89	0.576
B3	-359	4700	1131	630.2	804.5	21.14	31.25	42.33	306.9	65.3	20.91	0.497
B4	-305	5250	1149.8	622.7	722.2	23	33.65	41.1	303.4	61.4	ND	0.48
B5	-327	5270	1264.8	636.5	726.2	23.65	35.86	43.07	315.4	61.7	15.4	3.1
B6	-360	5620	1359.0	580.7	674.6	23.36	36.45	42.93	313.6	63.4	15.9	3.20
B7	-325	11725	1119.8	518.3	565.7	24.72	35.59	41.57	303.9	51.6	1.1	11.16
B8	-311	11210	1350.2	391.4	475.6	28.75	40.3	44.88	330.2	65.8	1.8	17.3

Table C-3. BH-STDwFE bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
BH-STDwFE	C1	10/25/16	4	22.7	12410	8270	11790	N/A	9.07	7322.16
BH-STDwFE	C2	10/29/16	8	24.5	13110	8750	12455	N/A	8.93	6458.62
BH-STDwFE	C3	11/2/16	12	21.2	13670	9100	12987	N/A	8.87	6738.81
BH-STDwFE	C4	11/7/16	17	19.6	13980	9320	13281	6060	8.72	7118.31
BH-STDwFE	C5	11/10/16	20	19.1	13800	9200	13110	10640	8.67	6692.7
BH-STDwFE	C6	11/15/16	25	21.5	13890	9260	13196	5640	8.58	6735.26
BH-STDwFE	C7	11/20/16	30	19	13530	9160	12854	16360	8.56	6761.86
BH-STDwFE	C8	11/30/16	40	22.9	13900	9260	13205	9260	8.53	6767.18

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO ₄ ²⁻ ICP (mg/L)	SO ₄ ²⁻ IC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	NH ₃ -N (mg/L)
C1	N/A	2060	593.2	508.3	869.5	14.8	40.3	39.6	239.0	67.4	18.27	N/A
C2	N/A	6950	1139.4	532.7	873.7	22.8	27.6	34.5	255.9	69.0	21.82	0.464
C3	-324	7690	1244.2	670.4	865.5	26.8	33.24	40.03	317.3	63.9	22.20	0.546
C4	-316	8370	1193.2	694.7	835.5	28.78	38.06	41.16	330.5	62.8	ND	0.396
C5	-337	5140	1279.4	676.4	800.3	27.84	37.24	40.91	323.4	62.0	15.9	2.06
C6	-220	5130	1283.4	625.3	716.0	29.55	39.63	41	322.9	61.6	16.6	2.97
C7	-341	12095	1195.2	549.1	622.8	31.13	39.45	40.93	311.4	54.4	3.3	9.47
C8	-309	11150	1333.2	419	517.3	34.77	44.67	42.88	327.9	77.0	4.4	23.8

Table C-4. BH-NC bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
BH-NC	D1	10/25/16	4	22.5	2000	1340	1900	N/A	8.04	940.39
BH-NC	D2	10/29/16	8	24.4	2390	1590	2271	N/A	7.5	445.56
BH-NC	D3	11/2/16	12	21.2	2720	1810	2584	N/A	7.65	574.57
BH-NC	D4	11/7/16	17	19.5	3320	2210	3154	1640	7.56	842.1
BH-NC	D5	11/10/16	20	19	3680	2460	3496	3220	7.58	1049.13
BH-NC	D6	11/15/16	25	21.5	8150	5440	7743	1720	8.75	4518.55
BH-NC	D7	11/20/16	30	N/A	N/A	N/A	N/A	N/A	N/A	N/A
BH-NC	D8	11/30/16	40	N/A	N/A	N/A	N/A	N/A	N/A	N/A

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO₄²⁻ ICP (mg/L)	SO₄²⁻ IC (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	Na⁺ (mg/L)	K⁺ (mg/L)	Cl⁻ (mg/L)	PO₄³⁻ (mg/L)	NH₃-N (mg/L)
D1	N/A	1570	1397.2	515.6	899.0	101.3	62.6	22.6	73.5	29.5	ND	N/A
D2	N/A	4090	1787.4	561.8	885.6	113.5	69.5	18.0	80.4	24.4	15.89	0.316
D3	-171	3080	2012	638.5	882.5	107.3	75.03	19.52	97.05	23.6	18.49	0.311
D4	-263	4020	1756.2	578.5	741.5	103.1	72.81	19.13	98.45	17.7	ND	0.295
D5	-218	3090	1704.6	648.8	710.3	119.1	84.69	21.63	109.1	16.9	13.8	0.487
D6	-185	4800	1372.2	596.9	686.9	91.23	65.64	20.69	105	29.6	14.9	0.51
D7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
D8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table C-5. OF-STD bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
OF-STD	E1	10/25/16	4	22.4	12710	8480	12075	N/A	8.99	7077.27
OF-STD	E2	10/29/16	8	24.7	13160	8770	12502	N/A	8.9	6809.75
OF-STD	E3	11/2/16	12	21.9	13650	9110	12968	N/A	8.84	7341.76
OF-STD	E4	11/7/16	17	19.6	13930	9290	13234	3140	8.75	6309.65
OF-STD	E5	11/10/16	20	19.2	14000	9340	13300	8540	8.69	6270.64
OF-STD	E6	11/15/16	25	21.6	14040	9340	13338	6500	8.6	6479.9
OF-STD	E7	11/20/16	30	19.1	13910	9240	13215	15020	8.58	6458.62
OF-STD	E8	11/30/16	40	23.1	14240	9510	13528	9660	8.52	6174.88

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO ₄ ²⁻ ICP (mg/L)	SO ₄ ²⁻ IC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	NH ₃ -N (mg/L)
E1	N/A	1770	556.2	836.8	1561.0	17.8	62.1	43.2	230.6	76.9	17.85	N/A
E2	N/A	4400	1053.2	797.4	1551.9	17.6	46.1	36.9	217.5	81.9	16.88	0.365
E3	-350	4500	1185.2	1111	1568.2	21.94	62.48	46.33	292.9	78.7	18.90	0.388
E4	-342	5240	1166.4	1047	1407.3	22.17	61.29	43.69	278	74.5	ND	0.318
E5	-310	4930	1271	1143	1420.8	23.73	69.01	48.5	305.6	75.0	15.2	1.83
E6	-338	5315	1376.4	1118	1400.9	24.3	69.04	47.92	302.3	74.2	15.0	3.18
E7	-318	12205	1268.6	1002	1307.7	23.43	67.25	45.46	287.2	65.9	0.9	11.58
E8	-327	11560	1313.0	893.9	1092.0	26.22	72	46.88	297	90.4	1.5	24.25

Table C-6. OF-NS bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
OF-NS	F1	10/25/16	4	22.5	12520	8330	11894	N/A	8.96	6506.5
OF-NS	F2	10/29/16	8	24.4	12940	8610	12293	N/A	8.86	6213.89
OF-NS	F3	11/2/16	12	21.2	13210	8790	12550	N/A	8.82	6299.01
OF-NS	F4	11/7/16	17	19.5	13440	8970	12768	2960	8.73	6061.38
OF-NS	F5	11/10/16	20	19	13170	8780	12512	13380	8.67	5767
OF-NS	F6	11/15/16	25	21.4	13260	8830	12597	9380	8.56	5983
OF-NS	F7	11/20/16	30	18.6	12910	8610	12265	22620	8.58	5926.61
OF-NS	F8	11/30/16	40	23.1	13170	8780	12512	18160	8.52	5671.24

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO ₄ ²⁻ ICP (mg/L)	SO ₄ ²⁻ IC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	NH ₃ -N (mg/L)
F1	N/A	2140	562.4	804.3	1513.7	18.3	47.5	39.4	239.5	72.8	16.71	N/A
F2	N/A	3860	1105.6	862.3	1610.3	20.4	46.0	40.8	253.7	78.2	17.75	0.464
F3	-355	5310	1129.4	1085	1560.8	22.32	54.57	46.04	308.5	77.8	19.55	0.498
F4	-355	6090	1112.8	1151	1451.1	23.89	60.62	49.07	326.1	75.4	ND	0.414
F5	-344	5460	1165.2	1086	1388.6	22.99	58.75	46.96	307.8	72.3	13.7	2.3
F6	-357	5140	1238.6	1100	1320.5	25.1	64.28	49.76	324.6	73.4	14.1	6.69
F7	-333	13330	1219.8	993.3	1195.1	26.6	66.93	49.28	312.7	64.2	0.9	14.15
F8	-351	11940	1168.4	727.8	879.7	26.48	62.99	44.98	291.2	84.3	2.7	23.45

Table C-7. OF-STDwFE bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
OF-STDwFE	G1	10/25/16	4	22.4	12480	8320	11856	N/A	9.09	7935.67
OF-STDwFE	G2	10/29/16	8	24.6	13820	9210	13129	N/A	8.94	7143.85
OF-STDwFE	G3	11/2/16	12	21.2	14140	9440	13433	N/A	8.93	7075.75
OF-STDwFE	G4	11/7/16	17	19.4	14440	9610	13718	5560	8.85	6990.63
OF-STDwFE	G5	11/10/16	20	18.9	14260	9520	13547	10200	8.76	6745.9
OF-STDwFE	G6	11/15/16	25	21.4	14380	9590	13661	9960	8.65	6618.75
OF-STDwFE	G7	11/20/16	30	18.5	14040	9360	13338	19260	8.59	6043.65
OF-STDwFE	G8	11/30/16	40	23	14220	9480	13509	16720	8.51	6433.79

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO ₄ ²⁻ ICP (mg/L)	SO ₄ ²⁻ IC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	NH ₃ -N (mg/L)
G1	N/A	1520	524.8	906.3	1582.2	12.9	85.7	44.4	256.9	75.7	15.45	N/A
G2	N/A	4150	951.2	794.6	1566.5	18.3	45.4	36.8	223.3	74.8	19.24	0.403
G3	-361	4860	1169.6	1122	1624.4	21.07	57.35	46.3	303.9	73.0	19.10	0.462
G4	-336	4920	1009.2	1151	1535.9	21.09	60.42	46.8	308.2	76.0	ND	0.367
G5	-341	5110	1150.4	1188	1464.0	21.71	63.58	48.09	317.5	66.8	13.8	3.53
G6	-356	7285	1307.8	1179	1467.6	23.42	66.59	48.9	320.4	74.6	15.1	6.46
G7	-323	14450	1202.0	1019	1317.6	24.42	67.67	45.53	294.1	64.7	ND	14.54
G8	-341	14680	1067.8	779.2	1012.0	24.07	64.8	41.32	267.9	83.3	ND	20.85

Table C-8. OF-NC bioreactor effluent characteristics.

REACTORID	ID	DATE	TIME (days)	TEMP. (°C)	SC (µS/cm)	TDS (meter - mg/L)	TDS (calc - mg/L)	TSS (mg/L)	pH	ALKALINITY (mg/L as CaCO3)
OF-NC	H1	10/25/16	4	22.3	2920	1950	2774	N/A	7.68	543.14
OF-NC	H2	10/29/16	8	24.6	3340	2230	3173	N/A	7.62	704.92
OF-NC	H3	11/2/16	12	21.2	7300	4870	6935	N/A	8.58	3479.35
OF-NC	H4	11/7/16	17	19.5	14120	9410	13414	2340	8.82	7421.56
OF-NC	H5	11/10/16	20	18.9	13570	9030	12892	2980	8.8	6618.22
OF-NC	H6	11/15/16	25	21.5	13180	8800	12521	2500	8.57	6074.05
OF-NC	H7	11/20/16	30	18.6	13110	8740	12455	2440	8.4	5871.63
OF-NC	H8	11/30/16	40	23.8	13280	8840	12616	1960	8.44	5664.15

ID	ORP (mV)	COD (mg/L)	TOC (mg/L)	SO ₄ ²⁻ ICP (mg/L)	SO ₄ ²⁻ IC (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	NH ₃ -N (mg/L)
H1	N/A	1890	1761.0	989.3	1772.8	174.6	141.8	24.5	101.0	38.7	15.78	N/A
H2	N/A	4220	1959.2	993.6	1778.0	183.0	144.4	23.5	100.5	38.0	18.01	0.39
H3	-300	8610	1711.6	1210	1767.6	166.9	152.9	27.4	125.2	41.3	18.51	0.288
H4	-213	4900	1093.8	1171	1540.2	21.34	87.62	27.03	127.1	48.0	ND	0.213
H5	-131	4390	1172.8	1192	1482.7	20.58	88.32	27.71	127.5	47.1	12.8	0.60
H6	-205	4775	1431.8	1162	1441.0	22.52	93.37	28.55	125.5	47.8	14.0	0.92
H7	-146	6965	1487.0	1089	1389.4	29.59	97.76	28.55	124.4	36.5	1.0	0.69
H8	-227	7035	1778.2	985.6	1160.1	40.68	108.4	27.53	119.3	56.2	1.2	9.375