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DEVELOPMENT OF MIXED MEDIA FILTRATION FOR STORMWATER RUNOFF TREATMENT

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Development of Mixed Media Filtration for Stormwater Runoff Treatment

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ABSTRACT

Stormwater runoff generated in urban areas can increase the risks of flooding and contaminate surface waters. Various contaminants carried by stormwater runoff can negatively affect the water quality of receiving water bodies. Many of the conventional stormwater best management practices are designed to control runoff volume and remove particles in the runoff. Conventional stormwater control methods are generally not effective in removing other pollutants such as microorganisms and nutrients. Media filtration using reactive materials is a promising treatment technology for removing different contaminants from stormwater runoff. The objectives of this project are to develop a low-maintenance, low-cost mixed-media filtration system for stormwater treatment and perform laboratory and field-scale studies to evaluate the performance of the mixed-media filtration system. A focus of this project is to identify filter materials that are effective for Escherichia coli (E. coli) removal from stormwater. Laboratory batch adsorption and column experiments were conducted to evaluate E. coli removal capacities of selected filter materials, including two natural minerals (limestone and zeolite) and two industrial byproducts (recycled steel chips and steel slag). Steel chips were identified as the most efficient material for E. coli removal though laboratory studies. A field scale mixed-media filter using steel chips and steel slag was constructed at a stormwater detention pond in a residential area of Brookings, SD. The results of the field study showed that the mixed media removed an average of 50% of the E. coli and an average of 42% of phosphate in the runoff during the three-month field experiment. Overall, the results of this project indicate that media filtration using recycled steel chips is an effective technology to remove E. coli and phosphate from stormwater runoff.

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1. EXECUTIVE SUMMARY

1.1 Introduction

Stormwater runoff is generated from rain and snow melt events that flow over land or impervious surfaces. Population growth and urbanization have significantly altered the landscape and increased the impervious surface areas. Increased stormwater runoff can increase the risks of flooding. At the same time, stormwater runoff from urban areas has been found to carry large amounts of pollutants, such as heavy metals, nutrients, suspended solids, organic substances, and microorganisms. These contaminants in stormwater runoff present high risks to aquatic ecosystems and public health. The expansion of urbanization will likely increase the contamination of surface water bodies in the future. Therefore, it is important to understand the source and transport of urban stormwater and develop appropriate management tools to reduce the impact of runoff on natural water resources.

Different best management practices (BMPs) have been developed to control the pollutants in stormwater runoff. The removal of runoff contaminants can be achieved by a variety of technologies including detention/retention basins, bioinfiltration basins, vegetative swales, constructed wetlands, and other engineered treatment systems. However, many of the conventional BMPs are designed to control runoff volume and remove particles in the runoff. These conventional BMPs are generally not effective in removing other pollutants such as microorganisms, nutrients, and heavy metals. Infiltration-type stormwater treatment systems are able to remove different contaminants, but these systems typically require a large operating footprint and have the risk of contaminating groundwater. There is a need to develop low-cost, low-maintenance, and effective BMPs that can remove multiple contaminants in stormwater runoff.

Media filtration has received increasing attention as an alternative stormwater BMP to remove particulate and dissolved pollutants from stormwater runoff using reactive filter materials such as sand coated with metallic hydroxide, zeolite, limestone, iron products, steel slag, woodchips, and tire crumbles. It has been shown that no single filter media could effectively remove all of the contaminants of concern in stormwater, and combinations of several of these filter media are necessary to achieve the removal of multiple contaminants. In addition, most stormwater filtration studies have focused on nutrients and heavy metals. There is a lack of information in the literature on the removal of microorganisms such as Escherichia coli (E. coli) by stormwater filtration technologies. E.coli has been widely used as an indicator microorganism for fecal contamination in stormwater runoff. The U.S. Environmental Protection Agency regulates E.coli levels in fresh recreational waters to limit the health risks of disease-causing pathogens.

The objectives of this project are to develop a low-maintenance, low-cost mixed-media filtration system for stormwater treatment and perform laboratory and field-scale studies to evaluate the performance of the mixed-media filtration system. A focus of this project is to identify filter materials that are effective for E. coli removal from stormwater. To achieve these objectives, laboratory batch and column experiments were conducted to evaluate E. coli removal capacities of four filtration materials. including limestone, zeolite, steel slag, and steel chips. After the laboratory study, steel chips and steel slag were selected as filtration materials to conduct a field-scale study. A mixed media filter using steel chips and steel slag were constructed at a stormwater detention pond in the City of Brookings, SD. The removal efficiencies of E. coli and phosphate by the mixed media filter at different storm events were determined.

1.2 Laboratory Study

Laboratory batch adsorption experiments were first conducted to evaluate E. coli removal capacities of selected filter materials, which included two natural minerals (limestone and zeolite) and two industrial byproducts (recycled steel chips and steel slag). E. coli adsorption isotherms and kinetics were determined for each of the four materials. The impact of initial concentrations, temperatures, pH, natural organic matter (NOM), and chloride concentrations on E. coli removal by the filter materials was also studied. The results of the batch adsorption experiments showed that the E. coli removal capabilities by the four materials were in the order of steel chips > steel slag > limestone and zeolite. The quantities of E. coli attached to steel chips were three orders of magnitudes higher than that of steel slag, and four orders of magnitudes higher than that of limestone and zeolite during the adsorption isotherm experiment. E. coli adsorption onto steel chips and steel slag was favored at high temperature, low pH, low NOM, and high chloride conditions. Steel chips and steel slag also showed low E. coli detachment percentages compared with limestone and zeolite during the E. coli desorption experiment.

Steel chips were identified as the most efficient material for E. coli removal during the batch adsorption experiments. Fixed-bed column experiments were conducted to determine E. coli removal capacities of steel chips under continuous flow conditions. Important filtration parameters, including initial concentrations, particle sizes, empty bed contact time (EBCT), and pH, were varied during the column experiments to encompass a wide range of operating conditions. Effects of NOM and intermittent flows on E. coli attachment and detachment were also investigated.

The E. coli removal by the fixed-bed steel chip columns under standard experimental conditions (chip size =1.0-2.0 mm, pH = 7.0, E. coli concentration = 10^6 MPN/mL, and EBCT =10 min) varied between 89.5% and 99.2% during the 72-hour operation. Smaller steel chip sizes, longer EBCT, lower initial E. coli levels, and lower pH values resulted in higher E. coli removal efficiencies in the steel chip columns. The presence of NOM interfered with E. coli adsorption and also promoted E. coli detachment from steel chips. Short-term intermittent flow temporarily decreased E. coli removal in the drained steel chip column, but the impact diminished quickly after the 30-minute operation. Short- and long-term intermittent flows did not affect E. coli removal in the undrained steel chip columns.

1.3 Field Scale Study

Recycled steel chips exhibited the highest E. coli removal capacity among the four tested filter materials. Steel slag showed the second best E. coli removal performance. Therefore, steel chips and steel slag were chosen to construct a mixed media filter for the field study. Steel chips were used as the main reactive filter materials and steel slag was used as the supporting material while providing additional removal capacity. A stormwater detention pond in a residential area in the City of Brookings, SD, was selected as the field study site. A mixed media filter was installed at the inlet of detention pond. The filter media were comprised of 25% large steel slag, 12.5% small steel slag, 50% large steel chips, and 12.5% small steel chips. Four storm events between July and September 2018 were monitored to determine the treatment efficiencies of the field scale filer. Filter influent and effluent samples were collected during each event to determine the removal of E. coli, phosphate, and others.

The results of the field scale filtration study showed that the mixed media filter removed an average of 50% of the E. coli and an average of 42% of phosphate in the runoff under the hydraulic retention times of 23-50 seconds. The mixed media maintained stable E. coli and phosphate removal efficiencies throughout the three-month field experiment. These results demonstrate that mixed media filtration using recycled steel chips and steel slag is an effective technology for removing E. coli and phosphate from stormwater under field conditions.

1.4 Recommendations

Media filtration is a promising technology to reduce contaminant levels in stormwater runoff. Filter materials evaluation and selection are critical to the application of stormwater filtration technologies. The use of practical and cost-effective materials that possess high contaminant removal capacities would promote the full-scale filtration applications in stormwater management. In this project, recycled steel chips exhibited high E. coli removal efficiencies through laboratory batch experiments, laboratory column experiments, and field scale filtration experiments. Recycled steel chips are readily available as an industrial byproduct at low cost. Steel chips also come with different sizes and shapes that can meet the needs of different hydraulic conditions. Therefore, we recommend that recycled steel chips can be used as a viable filter material for E. coli and phosphate removal in full-scale stormwater BMP applications.

Maintenance and longevity are two major concerns when using new filter materials for stormwater treatment. The mixed media filter with steel chips and steel slag showed stable E. coli and phosphate removal throughout the three-month field study. It is recommended that extended laboratory filtration studies and multi-year and multi-season field studies should be conducted to evaluate the longevity of steel chips for E. coli and phosphate removal. The mixing ratio of steel chips with other materials such as steel slag should also be evaluated in laboratory and field studies to determine the optimum media compositions that would maintain treatment performance and reduce filter clogging potentials.

2. INTRODUCTION

2.1 Stormwater Runoff

Stormwater runoff is generated from rain and snow melt events that flow over land or impervious surfaces, such as paved roads, parking lots, and building rooftops (EPA, 2018). Stormwater runoff can increase the risks of flooding and contaminate the receiving surface waters. Population growth and urbanization have significantly altered the landscape and consequently influenced surface water quality. The expansion of urban areas increases the impervious surface areas such as building roofs, parking lots, sidewalks, and roads. Those impervious surfaces do not allow water to penetrate the ground, increasing the percentage of precipitation that becomes runoff from about 10% in an undisturbed setting to around 55% in a fully urbanized setting, contributing to the increased flooding frequency and excessive streambank erosion (Paul and Meyer, 2001). At the same time, stormwater runoff from highways and urban areas contains large amounts of inorganic and organic pollutants, such as suspended solids, microorganisms, nutrients, and heavy metals. Contaminants carried into natural water bodies by stormwater runoff can significantly deteriorate water quality and cause public health concerns (House et al., 1993). According to a report published by United Nations (UN), the world population living in urban areas is expected to reach 6.3 billion by 2050 (UN, 2014). The expansion of urbanization will likely increase the stormwater runoff volume and the contamination of surface water bodies. Therefore, it is important to understand the source and transport of urban stormwater and develop appropriate management tools to reduce the impact of runoff on natural water resources.

2.2 Stormwater Pollutants

Stormwater runoff from urban areas has been found to carry large amounts of pollutants, such as heavy metals (e.g., copper [Cu], zinc [Zn], cadmium [Cd], nickel [Ni], and lead [Pb]), nutrients (phosphate and nitrate), suspended solids, organic substances, and microorganisms (viruses and bacteria). These pollutants can negatively affect surface water quality and public safety (House et al., 1993; Hatt et al., 2008; Tafuri and Field, 2012).

Excessive phosphorus and nitrogen inputs to surface waters is the primary cause of eutrophication and frequent harmful algal blooms. Algal blooms can clog waterways and prevent photosynthesis of the aquatic plants, leading to low dissolved oxygen (DO) and the loss of aquatic animal life (Smith et al., 1999). Fertilizer, excrement, and detergents are the main sources of phosphorus and nitrogen in stormwater (Mallin et al., 2009). Total suspended solids (TSS) is a parameter used to quantify suspended particles in runoff and it generally comes from soil erosion by wind, water, and agricultural activities. Large amounts of TSS in stormwater runoff can deposit in sensitive areas such as wetlands, wildlife preserves, streams, and lake bottoms, destroying the aquatic life habitat (Davis and McCuen, 2005). TSS can also block sunlight needed by aquatic plants (Carr and Neary, 2008; Kim et al., 2012). Heavy metals in water can be toxic to aquatic life and the presence of heavy metal in drinking water sources can threaten human health. The most common heavy metals in stormwater are cadmium, copper, lead, mercury, nickel, chromium, and arsenic (Mulligan et al., 2001). Heavy metals cannot be degraded naturally in the environment, instead they will be accumulated in fishes or plants and eventually transferred into humans by the food chain. Heavy metals in runoff usually come from a variety of human activities, including mining, vehicle emissions, tires, and motor oil factory (Wackernagel and Rees, 1998).

Microorganisms in stormwater include bacteria, viruses, and parasites. Disease-causing pathogens transmitted via drinking water are predominantly of fecal origin. E. coli has been used as an indicator microorganism for fecal contamination in stormwater runoff. E. coli are a large and diverse group of bacteria commonly found in the intestines of human and animals, and most E.coli are harmless. However, several strains, such as E.coli O157:H7, can cause severe health problems such as diarrhea, vomiting, and fever (Abuladze et al., 2008; Croxen et al., 2013). In the United States, illnesses and infections due to E. coli contamination are found to cost more than $405 million annually (Frenzen et al., 2005). The U.S. Environmental Protection Agency (U.S. EPA) set up an E. coli standard for fresh recreational waters (a geometric mean of 126 E. coli colony-forming unit [cfu] per 100 mL) to limit the health risks of disease-causing pathogens (Cho et al., 2010; EPA, 2012; Noble et al., 2003). E. coli can be transported into freshwater through stormwater runoff that passes through bird feces and wild and domesticated mammalian feces. Municipal sewer overflows are also considered as a major source of E. coli (Selegean et al., 2001).

South Dakota Department of Environment and Natural Resources (SDDENR) assessed about 5,916 stream miles in South Dakota from 2012 to 2017, and the results showed that 73.5% of assessed stream miles did not support one or more beneficial uses (SDDENR 2018). Nonsupport for fishery/aquatic life uses was caused primarily by total suspended solids from nonpoint sources and natural origin. Nonsupport for recreational uses was primarily caused by E. coli contamination from livestock and wildlife contributions. SDDENR also assessed 171 of the 575 lakes and reservoirs assigned recreation and/or fish life beneficial uses (SDDENR 2018). An estimated 84.3% of the assessed lake acreage did not support all assigned beneficial uses. One major cause is excessive algae growth due to nutrient enrichment from watershed scale nonpoint sources.

2.3 Stormwater Best Management Practices

Different best management practices (BMPs) have been developed to control the pollutants in stormwater runoff. The removal of runoff contaminants can be achieved by a variety of technologies, including detention/retention basins, bioinfiltration basins, vegetative swales, constructed wetlands, and other engineered treatment systems (Clark and Pitt, 2012). However, many of the conventional BMPs (e.g., detention ponds) are designed to control runoff volume and remove particles in the runoff. These conventional BMPs are generally not effective in removing other pollutants such as E. coli, nutrients, and heavy metals. Infiltration-type stormwater treatment systems are able to remove different contaminants, but these systems typically require a large operating footprint and have the risk of contaminating groundwater. There is a need to develop low-cost, low-maintenance, and effective BMPs that can remove multiple contaminants in stormwater runoff.

Media filtration has received increasing attention as an effective technology that can remove particulate and dissolved pollutants from stormwater runoff, using a relatively small footprint. Many low-cost filter materials have been evaluated for their potential for stormwater treatment. These materials include anthracite coal, sand, sand coated with metallic hydroxide, zeolite, limestone, iron products, steel slags, woodchips, sawdust, and tire crumbles; all of which possess good hydraulic properties and are readily available (Bailey et al., 1999; Lukasik et al., 1999; Hatt et al., 2008; Kim et al., 2010; Wium-Anderson et al., 2012; Reddy et al., 2014a). It has been shown that these low-cost filter materials can remove suspended solids, nutrients, microorganisms, and metals commonly found in stormwater runoff. However, studies also showed that no single filter media could effectively remove all of the contaminants of concern in stormwater (Wium-Anderson et al., 2012; Reddy et al., 2014b). Combinations of several of these filter media are necessary to achieve the removal of multiple contaminants.

Seelsaen et al. (2006) demonstrated that different sorption media mixes (sand, compost, zeolite, etc.) can be used as effective mediums for the treatment of dissolved metal contaminants commonly found in stormwater. Prabhukumar (2014) performed column experiments to evaluate the contaminant removal of individual media materials. The results showed that calcite was most efficient for nutrients and suspended solids removal, zeolite was highly effective in removing E. coli, and iron fillings were effective in removing nutrients and metals. Reddy et al. (2014b) showed that mixed-media filtration (calcite, zeolite, sand, and iron fillings) was effective for simultaneous removal of nutrients and heavy metals from stormwater runoff.

These studies suggest that mixed-media filtration systems using permeable reactive materials have great potential to remove multiple contaminants in stormwater runoff. Many studies have evaluated filter materials for nutrient and heavy metal removal from stormwater. However, there is a lack of information in the literature on the removal of microorganisms such as E. coli by stormwater filtration. More studies are needed to develop stormwater filtration technologies to improve the removal of E. coli from stormwater runoff.

2.4 Project Objectives

Many surface water bodies in South Dakota and other areas are impaired by sediment, nutrients, and bacteria from point and non-point sources. Stormwater runoff has been identified as a major source of contamination in surface waters. Mixed-media filtration is a highly promising treatment option that can reduce the concentrations of multiple contaminants in stormwater runoff generated from highways and urban areas. The objectives of this project are to develop a low-maintenance, low-cost mixed-media filtration system for stormwater treatment and perform laboratory and field-scale studies to evaluate the performance of the mixed-media filtration system. A focus of this project is to identify filter materials that are effective for E. coli removal from stormwater. The following three project tasks were conducted during this project to achieve the project objectives.

Task 1: Laboratory batch experiments were conducted to evaluate E. coli removal capacities of four filtration materials: limestone, zeolite, steel slag, and steel chips.

Task 2: Laboratory column experiments were conducted to determine factors that affect the E. coli removal by steel chips under continuous flow conditions.

Task 3: Steel slag and steel chips were selected as filtration materials to conduct a field-scale study. A mixed media filter using steel slag and steel chips was constructed at a stormwater detention pond in the City of Brookings, SD. The removal of phosphorus, nitrogen, and E. coli by the mixed media filter at different storm events were determined.

3. EVALUATION OF FILTER MATERIALS FOR E. COLI REMOVAL FROM STORMWATER

3.1 Introduction

Stormwater filters remove contaminants through physical straining and chemical reactions. Suspended particles can be effectively removed by sand filter through physical removal processes. However, physical processes are generally not effective at removing other contaminants such as nutrients and pathogens during stormwater filtration. Reactive filter materials are needed to remove those contaminants. The selection of filter media for stormwater treatment depends on several factors, such as the removal efficiencies of target contaminants and the physical and chemical properties of the materials. It is desirable to use cost-effective and readily available materials that require little or no maintenance during stormwater treatment. Good permeability is also important for the stormwater filter media. As the first task of this project, four filter materials were selected to evaluate their E. coli removal efficiencies using laboratory batch adsorption experiments. The four materials were limestone, zeolite, steel slag, and recycled steel chips. The goal of this task was to identify filter materials that possess high E. coli removal capacities.

3.2 Materials and Methods

3.2.1 Filter Materials

Limestone is a sedimentary stone composed of varying crystal forms of calcium carbonate ($CaCO_3$) (Aziz et al., 2001) and it was acquired from Martin Marita Limestone Co, Inc. Natural zeolite is formed in basaltic lava and particular rocks exposed to moderate geologic temperature and pressure. The natural zeolite from Bear River Zeolite Co, Inc. was used for this study. Recycled steel chips are produced by cutting, shaping, drilling, and finishing steel products. Steel chips made from carbon steel were obtained from a metal machining factory in Sioux Falls, SD. Electric arc furnace steel slag is a byproduct of steelmaking and typically produced through the blast furnace. Slag is usually a mixture of metal oxides and silicon dioxide. The steel slag was collected from Nucor Steel (Norfolk, Nebraska).

All filter materials were sieved to the size range of 1-2 mm. After sieving, each filter material was washed with distilled water to remove any dust or very fine particles that can cause interference in adsorption experiments. Steel chips were also washed with phosphate free soap to remove any possible oil on the surface. Then materials were air-dried. During the drying process, the steel chips were oxidized, forming a layer of rust on the surface. Figure 3.1 presents a picture of the four materials.

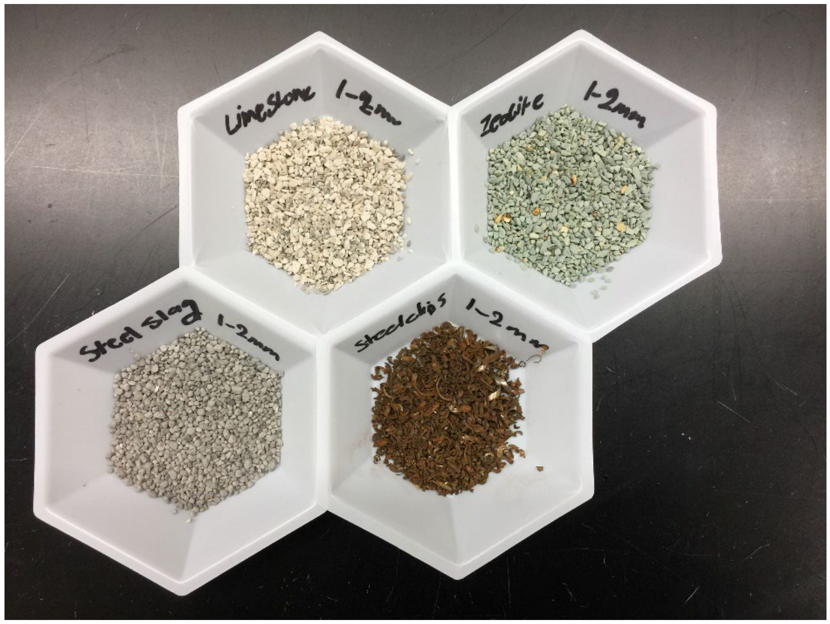

Figure 3.1 Filter materials used for batch experiments
(top: limestone and zeolite; bottom: steel slag and steel chips)

3.2.2 E. Coli Preparation

An E. coli strain ATCC 35218 (American Type Culture Collection) was used as bacteria culture in this study. This E. coli strain was incubated in a 100 mL Luria Broth Base (Thermo Fisher Scientific, 10 g/L of peptone, 10 g/L of sodium chloride, 5 g/L of yeast extract) at 37ºC in a temperature-controlled shaker. The culture was shaken at 150 rpm for 24 hours, then the cells were centrifuged to remove growth media and washed with buffer solution three times before re-suspending in buffer solution. The buffer solution was prepared by dissolving 1.0 mole $NaHCO_3$ and 0.01 mole KCl in one liter of distilled water. The pH value of the buffer solution was adjusted to 7 using 1.0 mole/L H_2SO_4 solution. A spectrophotometer (Model DR400, Hach) was used for measuring E. coli cell concentration in buffer solution. Serial dilutions were used to bring the E. coli concentration to the level of 1×10^4 to 1×10^7 MPN (most probably number) per mL as initial E. coli concentrations for the batch experiments. IDEXX Quanti-Tray 2000 method was used to measure E. coli concentrations in samples. All containers used for E. coli culture were autoclaved prior to use.

3.2.3 Adsorption Isotherms

Batch adsorption experiments were conducted to obtain E. coli adsorption isotherms for each of the four materials. Different materials masses (0.1-16 g) were used for the isotherm experiments. Each material was placed in a 250 mL Erlenmeyer flask containing a 100 mL buffer solution with an initial E. coli concentration of 10^4 MPN/mL for steel slag, limestone, and zeolite, and 10^7 MPN/mL for steel chips. A flask with 100 mL E. coli solution without any absorbent was prepared as a control. Flasks were placed in a shaker and were continuously shaken at 100 rpm for 24 hours at 20°C. After 24 hours, flasks were removed from the shaker and each sample was analyzed for E. coli concentration using the IDEXX method. The following steps were involved in E. coli analysis with the IDEXX Quanti-Tray/2000. First, samples were diluted to below the detection limit of 2400 MPN/100 mL and placed into a 100 mL IDEXX vessel containing a dechlorination chemical. Second, one packet of Colilert reagent (IDEXX) was added to the sample bottle. After that, the solution was poured into the incubation tray and sealed by a Quanti-Tray sealer (Cat WQTs2X-115). The sealed tray was then placed in a 45°C incubator for 24 hours. Last, the E. coli results were determined based on the number of positive wells of the Quanti-Tray. All experiments were conducted in duplicate to ensure the accuracy of the experiments. The results of the duplicate experiments are expressed as average values and standard deviations.

The equilibrium adsorption capacity, q_e (MPN/g), was calculated by the following equation

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad \text{(Equation 3.1)}$$

where C_0 and C_e are the initial and equilibrium E. coli concentrations (MPN/mL), V is the volume of the solution (mL), and m is the mass of the adsorbent (g).

The Freundlich isotherm model was used for fitting the E. coli adsorption experimental data. The linearized form of the Freundlich model can be described as:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad \text{(Equation 3.2)}$$

where K_F and n are Freundlich constants indicative of the adsorption capacity and adsorption intensity, respectively.

3.2.4 Adsorption Kinetics

E. coli adsorption kinetics were evaluated at an initial concentrations of 10^7 MPN/mL for steel chips, and 10^4 MPN/mL for steel slag, limestone, and zeolite, respectively, at 20°C. Samples were collected at different time intervals of 30, 60, 120, 360, 720, and 1,440 minutes for E. coli measurement. The adsorption data were fitted to pseudo first-order and second-order kinetic models. The pseudo first-order kinetic model is shown below.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \qquad \text{(Equation 3.3)}$$

where q_t is the adsorption capacity at time t (MPN/g), t is the shaking time (h), and k_1 is the first-order equilibrium rate constant (h^{-1}). The pseudo second-order kinetic model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad \text{(Equation 3.4)}$$

where k_2 is the second-order equilibrium rate constant (g/MPN-h).

3.2.5 Factors Affecting E. Coli Adsorption

After the isotherm and kinetics adsorption tests, one gram of steel chips, steel slag, limestone, and zeolite was used to evaluate the E. coli removal capacities at different initial E. coli concentrations of 10, 100, 1,000, and 10,000 MPN/mL. Samples were placed in 250 mL flasks and continuously shaken at 100 rpm for two hours at 20°C. Then flasks were removed from the shaker and analyzed to obtain E. coli removal efficiency.

Temperature, pH, organic matter, and salt concentration are several common environmental factors that could affect E. coli removal during stormwater filtration. Steel chips and steel slag were selected to evaluate the impact of these parameters on the E. coli removal. E. coli adsorption experiments were conducted at different temperatures (5, 20, 30°C), pH values (5, 7, and 9), natural organic matter (0, 5, and 20 mg C/L), and KCl concentrations (0, 100, and 1,000 mg Cl/L) for an initial E. coli concentration of 10^4 MPN/L for two hours. One gram of each material and 100 mL sample were used for this set of experiments.

3.2.6 E. Coli Desorption Experiment

The E. coli removed during stormwater filtration can be detached from the filter media during intermittent flow conditions. The detachment of E. coli from the media can deteriorate the treatment performance and cause E. coli spikes in the treated effluent. A batch desorption experiment was conducted to evaluate E. coli detachment from the four materials. First, E. coli was loaded to one gram of each material in 100 ml samples with an initial concentration of 10^7 MPN/L for steel chips and 10^4 MPN/L for steel slag, limestone, and zeolite. After samples were shaken at 100 rpm for 24 hours at 20ºC, E. coli concentrations were measured to determine the quantities of E. coli attached to each material. After that, each flask was decanted, and 100 mL of distilled water was added to the sample. The flasks were then shaken for 24 hours at 100 rpm. E. coli samples were taken at different time intervals of 30, 60, 120, 360, 720, and 1,440 minutes. The desorption ratios were calculated by comparing the detached E. coli with the total adsorbed E. coli before the desorption experiment.

3.2.7 Continuous Flow Column Experiment

Although batch adsorption experiments are often used to determine adsorption isotherms and kinetics, continuous flow column experiments are more appropriate to simulate the real stormwater filtration conditions. A column experiment was conducted to verify the results obtained from the batch E. coli adsorption experiments. Four Omnifit® fixed-bed glass columns with 1.5 cm inner diameter and 15 cm height were used as column reactors. The masses of 30, 34, 27.5, and 18.6 grams of steel chips, steel slag, limestone, and zeolite were placed into the columns to achieve a bed height of 10 cm. Figure 3.2 shows the column experimental setup.

Figure 3.2 E. coli column adsorption experimental setup

A four channel peristaltic pump was used to pump the influent from an influent tank to the four column reactors. The influent E. coli concentration was maintained in a range of 1.1×10^4 - 1.4×10^4 MPN/mL. A pumping rate of 1.76 mL/min was used to achieve an empty bed contact time (EBCT) of 10 minutes. The EBCT in the column is calculated from the ratio of bed volume (mL) to the flow rate (mL/min). The column experiment was conducted for five days, and the effluent samples were taken every day for E. coli measurements.

3.3 Results and Discussion

3.3.1 Adsorption Isotherms

The E. coli adsorption data for the four materials were fitted with the Freundlich isotherm model. The E. coli adsorption results at different equilibrium concentrations are presented in Figure 3.3. Steel chips showed the highest E. coli adsorption capacities among the four materials. The quantities of E. coli attached to steel chips were generally 3 orders of magnitudes higher than that of steel slag and 4 orders of magnitudes higher than that of limestone and zeolite. Steel slag was the second best material for E. coli removal. Limestone and zeolite were similar in E. coli removal efficiencies and showed the lowest E. coli adsorption capacities. These batch adsorption results suggest that the E. coli removal capabilities by the four materials at different equilibrium concentrations were in the order of steel chips > steel slag > limestone and zeolite.

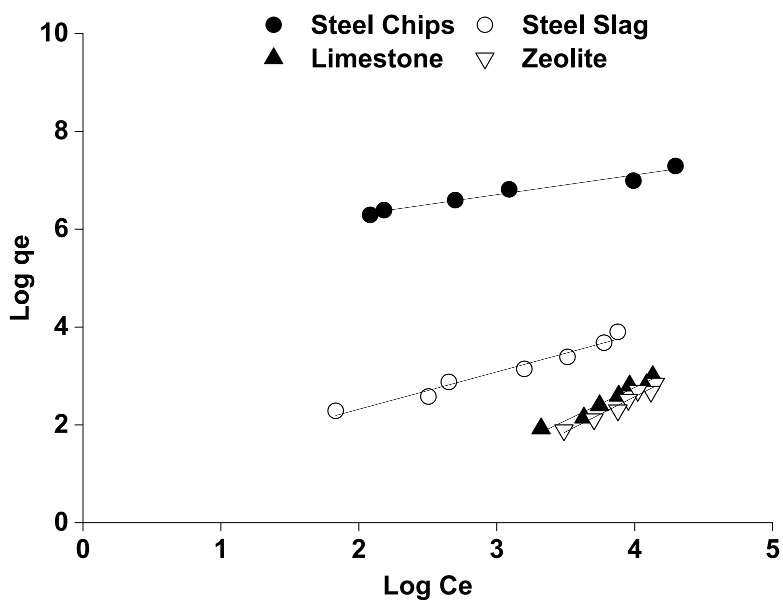

Figure 3.3 Freundlich isotherms for E. coli adsorption by the filter materials

Table 3.1 shows the Freundlich isotherms modeling results. The resulting model coefficients (R^2) varied between 0.959 and 0.968. Therefore, E. coli adsorption onto the four materials can be reasonably described by the Freundlich isotherms. This suggests that the adsorption of E. coli by these materials can be characterized by the formation of a multilayer adsorption of bacteria cells along the surface of the adsorbents (Yousef et al., 2011). The Freundlich isotherm constant (K_F) indicates the adsorption capacity. It can be seen from Table 3.1 that the K_F of steel chips was much higher than the K_F of steel slag, which was again much higher than the K_F of limestone and zeolite. These modeling results confirm the relative E. coli removal capacities of the four materials tested in this study. Hydrophobic attraction and electrostatic interaction are two forces that affect E. coli adsorption onto filter materials (An et al., 2015). E. coli cells are typically negatively charged in aqueous solutions. Therefore, filter materials that have more positively charged sites on the surface will adsorb more E. coli. The high E. coli removal capacity exhibited by steel chips may be attributed to the formation of large amounts of positively charged iron oxides on the surface. Steel slag also contains various iron and aluminum species that can contribute to E. coli attachment. It can be inferred from this adsorption experiment that limestone and zeolite have much fewer positively charged sites on the surface for E. coli attachment than steel chips and steel slag.

Table 3.1 Freundlich isotherm parameters for E. coli attachment

Material	Temp. (°C)	Freundlich isotherm		
		K_F (h^{-1})	1/n	R^2
Steel Chips	20	311659.2348	0.40	0.966
Steel Slag		6.2063	0.76	0.968
Limestone		0.0023	1.35	0.963
Zeolite		0.0007	1.44	0.959

3.3.2 Adsorption Kinetics

Figure 3.4 shows the amounts of E. coli adsorbed onto each materials at different reaction times during the 24-hour period. Steel chips showed high rates of E. coli adsorption and reached equilibrium conditions after six hours. Other materials reached equilibrium conditions after 12-hour adsorption. The E. coli adsorption kinetic data were fitted to pseudo-first-order and pseudo-second-order models. The modeling results are presented in Table 3.2. Second-order model fitted the steel chips data better than the first-order model as evidenced by the correlation coefficients (R^2). For the other three materials, the first-order model better described the E. coli adsorption kinetics. The calculated half-lives for E coli adsorption onto steel chips were much lower than steel slag, limestone, and zeolite, suggesting fast E. coli attachment onto the steel chip surface.

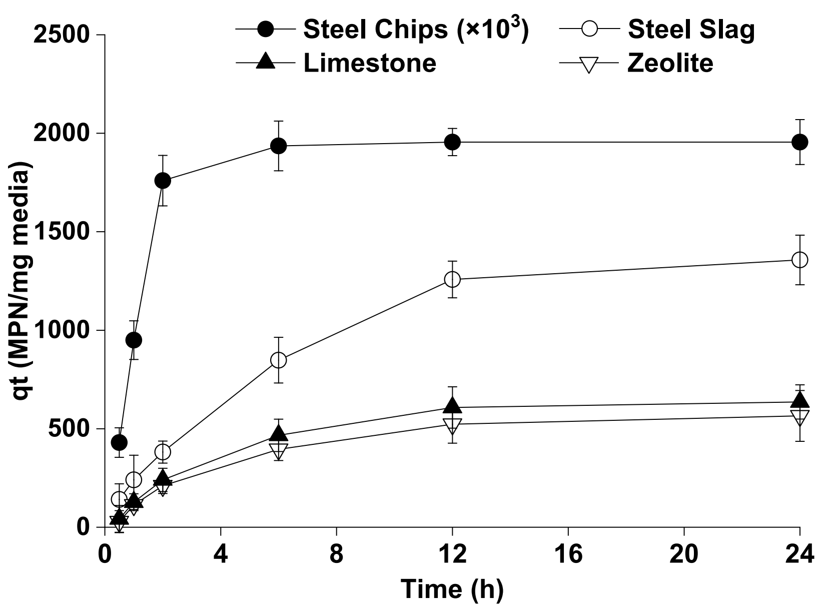

Figure 3.4 E. coli adsorption by the filter materials at different times

Table 3.2 Kinetic parameters for E. coli adsorption

Material	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (h^{-1})	R^2	Half-life (h)	k_2 (mg/MPN h)	R^2	Half-life (h)
Steel Chips	1.781	0.953	0.90	0.00000051	0.995	0.95
Steel Slag	0.479	0.995	3.33	0.00008851	0.990	6.34
Limestone	0.621	0.993	2.57	0.00022069	0.946	5.66
Zeolite	0.521	0.997	3.06	0.00018640	0.873	7.14

3.3.3 Factors Affecting E. Coli Adsorption

Figure 3.5 illustrates the effect of different initial E. coli concentrations on the removal efficiencies of filter materials. Increasing E. coli concentrations gradually decreased the removal percentages for steel slag, limestone, and zeolite. However, varying initial concentrations had little impact on E. coli removal by steel chips. The E. coli removal percentages for steel chips, steel slag, limestone, and zeolite were decreased by 4.4%, 43.8%, 43.2%, and 41.9%, respectively, when the cell concentration increased from 10 to 10,000 MPN/mL. This indicates that steel chips can maintain high E. coli removal efficiencies at different concentrations. This is important for field application of stormwater filtration technology since the E. coli concentration can vary substantially during storm events.

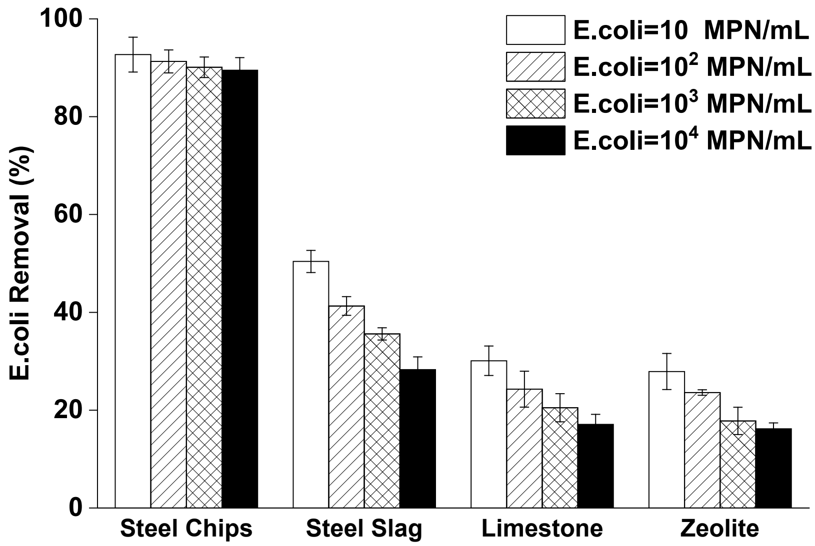

Figure 3.5 Effect of initial concentrations on E. coli adsorption

Figure 3.6 presents the impact of temperature, pH, NOM, and KCl on E. coli removal percentages by steel chips and steel slag. Moderate reductions (5.3%-13.0%) in E. coli removal were observed when the temperature decreased from 30 to 20ºC. When the temperature further decreased to 5ºC, both materials showed substantial reductions (61.7%-75.8%) in E. coli removal. It is clear the low temperature at 5ºC reduced the E. coli activities and inhibited the attachment of E. coli to adsorbent surfaces. Ishii et al. (2005) also reported that low temperatures negatively affected E. coli retention on filter materials. The pH values also had appreciable impact on E. coli adsorption. The E. coli removal percentages gradually declined with increasing pH from 5 to 9. The pH impact can be explained by the change in hydroxide ion concentrations. Negative charged hydroxide ions would compete for the adsorption sites at the particle surface and reduce the available sites for E. coli attachment. The adsorbed hydroxide ions would also reduce the positive charge of the particle surface, thereby reducing attraction force between E. coli and material surface (Starosvetsky et al. 2012).

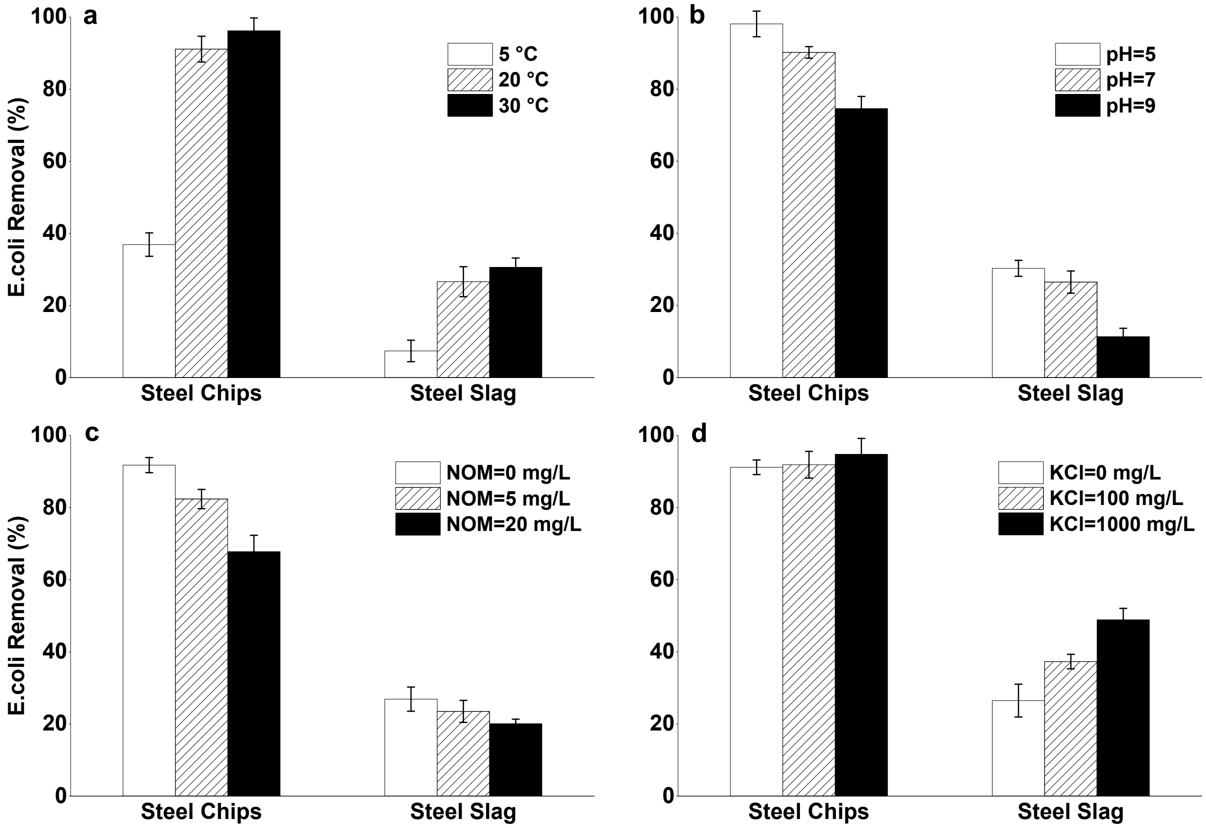

Figure 3.6 Effect of temperature, pH, NOM, and chloride on E. coli adsorption

Natural organic matter can also affect E. coli retention through competitive adsorption. Both steel chips and steel slag are rich in metal oxide species, which are known to adsorb organic compounds though ligand exchange and electrostatic attraction. The adsorbed NOM would reduce the removal of other contaminants. This NOM effect was observed for E. coli removal by steel chips and steel slag. The E. coli removal reduced by 26.1% and 25.1% for steel chips and steel slag, respectively, when increasing NOM from 0 to 20 mg C/L. Johnson and Logan (1996) reported similar reductions in bacteria attachment on quartz in the presence of Suwannee River dissolved organic matter. The impact of solution salinity (0-1,000 mg Cl/L) on E. coli removal was investigated and the results showed that high salt concentrations generally led to more E. coli attachment to filter materials. The removal of E. coli by steel chips only increased by 3.6 percentage points when increasing chloride concentration from 0 to 1,000 mg Cl/L. This may be because steel chips achieved nearly compete E. coli removal in the absence of chloride. Therefore, adding salt did not lead to a large improvement in removal. The impact of salt addition was more pronounced for steel slag, and the E. coli removal improved from 26.5% to 48.9% when increasing chloride concentration from 0 to 1,000 mg Cl/L. Adding salts to water will increase the solution ionic strength, which can compress the electrical double layer of the particles. This will decrease the repulsive forces and increase attractive forces between E. coli and filter materials, resulting in high E. coli removal.

3.3.4 Desorption of E. Coli

The results of the E. coli desorption experiment are presented in Figure 3.7. The ability to keep previously adsorbed E. coli on the filter media is critical to the success of field-scale filters. Over a period of 24 hours, steel chips, steel slag, limestone, and zeolite desorbed 0.02%, 0.40%, 3.11%, and 2.73% of the attached E. coli cells, respectively. E. coli release from steel chips is almost negligible compared with the total number of attached E. coli. This indicates that the binding forces between E. coli and iron oxides on the steel chip surface are strong enough to prevent the E. coli detachment. Steel slag also exhibited a low E. coli detachment percentage. Relatively high fractions of E. coli detached from the surfaces of limestone and zeolite, indicating generally weak adsorption strength between E. coli and these two materials.

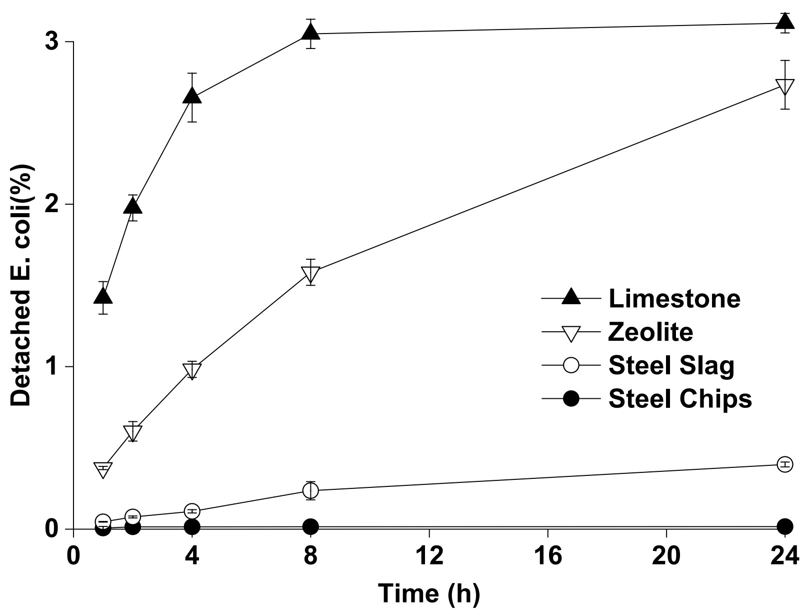

Figure 3.7 E. coli detachment from the filter materials

3.3.5 Column Experiment Results

The breakthrough curves during continuous flow column filtration experiments are shown in Figure 3.8. The ratio between effluent E. coli and effluent E. coli (C/C_0) reached 3.35%, 55.85%, 73.16%, and 85.72% for steel chips, steel slag, limestone, and zeolite, respectively, after the two-hour column operation. The corresponding E. coli removal efficiencies are similar to the batch adsorption experiments. The effluent E. coli concentrations for the four materials increased with increasing operating time. Limestone and zeolite reached adsorption exhaustion conditions ($C/C_0 > 95\%$) after four days and steel slag showed exhaustion after 12 days. Steel chips showed a very different E. coli breakthrough pattern compared with other filter materials. The effluent E. coli ratio (C/C_0) from the steel chip column gradually increased to 10.25% after a one-day operation. After that, the E. coli breakthrough curve leveled off and the ratio of C/C_0 varied from 10.42% to 10.89% between two and 12 days. The steel chip filter maintained high E. coli removal up to 12 days of operation. It is possible that dissolved oxygen in water continued to oxidize the steel chip surface to form a new adsorption site for E. coli, thereby achieving long-term stable removal efficiencies.

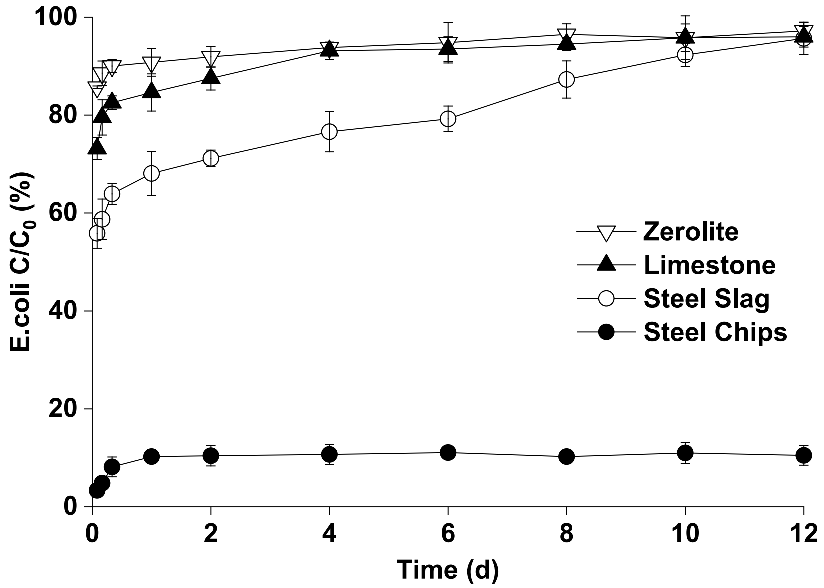

Figure 3.8 Continuous flow column filtration experiment for E. coli removal

3.4 Conclusions

The goal of this project task was to evaluate filter materials for E. coli removal during stormwater filtration. Two industrial products (recycled steel chips and steel slag) and two natural minerals (zeolite and limestone) were selected as filter materials for E. coli removal. Batch adsorption experiments were conducted to determine the E. coli adsorption isotherms and kinetics of the four materials. The impact of initial E. coli concentrations, temperature, pH, NOM, and chloride concentrations on E. coli removal was also investigated. A desorption experiment was conducted to evaluate E. coli detachment potentials of the four materials. A column filtration experiment was also conducted to determine E. coli removal characteristics of the four filter materials under continuous flow conditions.

The results showed that the E. coli removal capabilities by the four materials were in the order of steel chips > steel slag > limestone and zeolite. The quantities of E. coli attached to steel chips were 3 orders of magnitudes higher than that of steel slag, and 4 orders of magnitudes higher than that of limestone and zeolite during adsorption isotherm experiment. Steel chips also exhibited good E. coli removal at different initial E. coli concentrations. E. coli adsorption onto steel chips and steel slag was favored at high temperature, low pH, low NOM, and high chloride conditions. Steel chips and steel slag showed low E. coli detachment percentages during the desorption experiment, whereas appreciable amounts of E. coli detached from limestone and zeolite. The continuous flow column experiment confirmed the relative E. coli capacities of the four materials. Overall, steel chips demonstrated excellent E. coli removal under various experimental conditions during the batch adsorption experiments.

4. LABORATORY FIXED-BED COLUMN EVALUATION OF E. COLI REMOVAL BY STEEL BYPRODUCTS

4.1 Introduction

Continuous flow fixed-bed column experiments are widely used to evaluate the removal of water contaminants using filtration technologies. Fixed-bed column experiments are able to determine contaminant removal efficiencies under dynamic flow conditions, which can resemble real stormwater treatment systems. Steel chips demonstrated high E. coli adsorption capacities during the batch adsorption experiments. As a recycled steel byproduct, steel chips are cost effective materials that are locally available for environmental applications. Steel chips also come in different forms and sizes that can fit the need of different hydraulic conditions for stormwater filters. Fixed-bed column experiments were conducted in this project task to evaluate E. coli removal by steel chips under continuous flow conditions.

4.2 Materials and Methods

4.2.1 Filter Materials

The steel chips (1018 carbon steel), produced through grinding, drilling, or milling of finished iron products, were obtained from Prairie Manufacturing, LLC (Sioux Falls, SD). After collection, the steel chips were washed with phosphate-free soap to remove surface cutting fluids and allowed to air dry for 48 hours. Dried steel chips were then sieved into four groups based on the particle sizes (0.5-1.0, 1.0-2.0, 2.0-4.0, and 4.0-8.0 mm) before using. Figure 4.1 shows pictures of the four steel chips used for this study.

Figure 4.1 Pictures of the steel chips used for column experiments

4.2.2 Stormwater Samples

Synthetic stormwater with spiked E. coli cells were used for the column experiments. The synthetic stormwater was prepared by ultrapure water (18 mΩ-cm) produced by a Barnstead NANOpure system. Then 1 mM $NaHCO_3$ and 0.1 mM KCl were dissolved into the ultrapure water to resemble the real stormwater in terms of initial ionic strength. No nutritional elements were added to the synthetic stormwater to inhibit E. coli multiplication. The pH of the synthetic stormwater was adjusted to 7.0±0.1 with H_2SO_4.

Different volumes of cultured E. coli stock samples were added to the synthetic stormwater to achieve designated E. coli concentrations for the column experiments.

In addition to the synthetic stormwater, real stormwater runoff samples were also collected and evaluated for E. coli removal. Runoff samples were collected from two stormwater dentation ponds; one is located adjacent to a large parking lot and the other is located in a residential area. Both stormwater detention ponds are within the City of Brookings, SD. Table 4.1 shows the water quality of the two stormwater samples. Both samples had E. coli concentrations in the order of 10^2 MPN/mL.

Table 4.1 Water quality of collected stormwater

Stormwater	pH	Total Suspended Solid (mg/L)	DOC (mg/L)	E. coli (MPN/mL)
Parking Lot	6.9	37	1.94	91
Residential Detention Pond	7.1	55	2.83	102

4.2.3 Bacteria Preparation

Escherichia coli (ATCC 35218, American Type Culture Collection) was used as model bacteria in this study. E. coli was cultured in a 100 mL Luria Broth Base (LB, Thermo Fisher Scientific, 10 g/L peptone, 10 g/L sodium chloride, 5 g/L yeast extract) at 37°C and 150 rpm for 24 hours under aerobic conditions in a temperature controlled orbital shaker (Thermo Scientific MaxQ 4000). The cultured E. coli were then extracted from the LB media with a centrifuge (Thermo Scientific SorvallTM ST 8 Benchtop Centrifuge) and washed three times with buffer solution (1 mM $NaHCO_3$, 0.1 mM KCl, pH=7.0±0.1 using H_2SO_4) to remove any residual growth media. After harvest, E. coli were resuspended in a 100 mL buffer solution to achieve E. coli stock samples of 1.0-1.3×10^9 MPN/mL. The E. coli stocks were stored at room temperature before use.

4.2.4 Fixed-bed Column Reactors

Fixed-bed column reactors were built using glass chromatography columns (Omnifit, 15 cm length, 1.5 cm inside diameter). Steel chips in different size ranges (0.5-1.0, 1.0-2.0, 2.0-4.0, and 4.0-8.0 mm) were packed into separate columns to achieve a 10 cm packing height. The characteristics of the steel chips in the columns were tested according to the American Society of Testing and Materials (ASTM) standard testing procedures. Table 4.2 shows the characteristics of the steel chip columns.

Table 4.2 Characteristics of steel chip columns

Material	Size (mm)	Particle Density (g/cm^3)	pH	Packing Density (g/cm^3)	Porosity (%)
Steel chips	0.5-1.0	5.1	6.3	1.50	0.43
	1.0-2.0	5.2	6.3	1.35	0.52
	2.0-4.0	5.5	6.3	1.16	0.67
	4.0-8.0	5.7	6.3	0.94	0.75

a. Particle size ranges were determined by standard sieve analysis.
b. Particle densities were determined using the water displacement method.
c. Values of pH were obtained from a 1:1 by weight ratio of material and distilled water.
d. Packing densities were determined by the volume occupied by the mass of each material in the column reactor.

Figure 4.2 presents the experimental setup for the column experiments. A 20L glass container was used as the influent tank to keep stormwater samples. The influent sample was continuously mixed by a mechanical stirrer. Peristaltic pumps (Masterflex L/S) were used to pump the stormwater samples from the influent tank to the steel chip columns. The E. coli samples were pumped upward through the steel columns and the effluent samples were collected periodically to monitor the treatment performance.

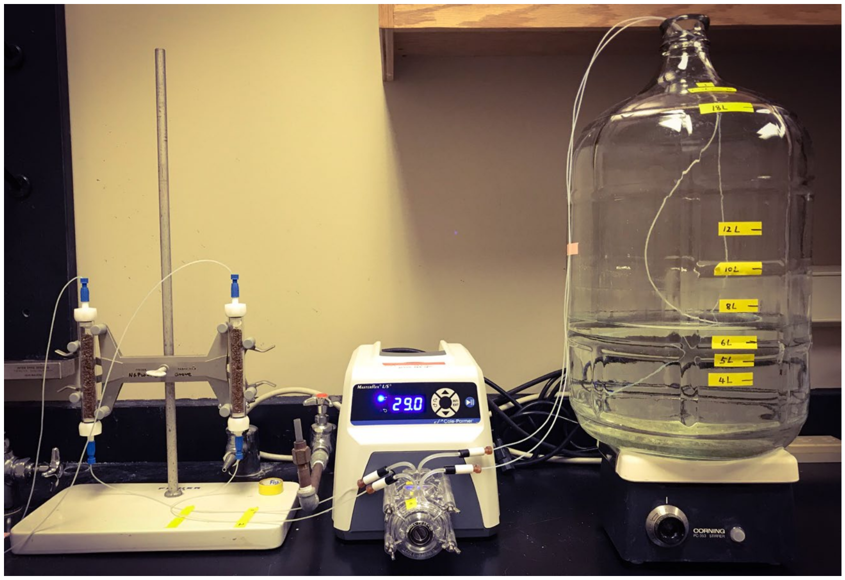

Figure 4.2 Experimental setup for the column experiments

4.2.4 Experimental Design

First, steel chip column experiments were conducted to evaluate E. coli removal under different steel chip sizes (0.5-1.0, 1.0-2.0, 2.0-4.0, and 4.0-8.0 mm), empty bed contact times (EBCT, 5, 10, 20 min), influent concentrations (10^2, 10^4, and 10^6 MPN/mL), and pH values (5, 7, and 9). These parameters were varied one at a time while other parameters are fixed. The standard experimental conditions were the following: steel chips size =1.0-2.0 mm, pH = 7.0, E. coli concentration = 10^6 MPN/mL, and EBCT = 10 min. For each condition, the influent sample was pumped through the columns for a total of 72 hours. The influent and effluent samples were taken simultaneously for analyzing E. coli concentrations.

Second, the impact of natural organic matter (NOM) on E. coli removal was studied using steel chip columns. Suwannee River Aquatic NOM (International Humic Substances Society, St. Paul MN, USA) was added to the synthetic stormwater to simulate a wide range of dissolved organic carbon (DOC) levels (0, 5, and 30 mg/L). The NOM impact experiment was conducted under standard column experimental conditions. The three column reactors were operated for 72 hours to determine the effect of NOM on E. coli removal efficiencies. After the experiment, steel chips samples from the three reactors along with raw steel chips were analyzed by scanning electron microscopy (SEM, Model Hitachi S-3400N, Santa Clara, CA) to investigate surface properties and E. coli attachment.

The impact of NOM on E. coli detachment from steel chips was also studied. E. coli samples were loaded to three steel chip columns under standard column experimental conditions for 72 hours. After that, the three columns were washed with ultrapure water containing 0, 5, and 30 mg C/L NOM, respectively, for 12 hours. The EBCT was controlled at 10 minutes. Effluent samples were collected at different time intervals and analyzed to calculate the total amount of detached E. coli from steel chips.

Third, short-term and long-term intermittent flow experiments were conducted to exam the effects of intermittent stormwater flow conditions on the E. coli attachment to steel chips. In the short-term intermittent flow experiment, a six-hour operation with a one-hour interval was used for a total of three cycles. In the long-term intermittent flow experiment, a three-day operation with a 14-day interval was used for a total of three cycles. Standard experimental conditions were used for these two experiments (steel chips size =1.0-2.0 mm, pH = 7.0, E. coli concentration = 10^6 MPN/mL, and EBCT =10 min). Two identical columns were used for each intermittent flow experiment, and one column was drained, and the other was kept saturated during the intervals.

Last, E. coli removal from real stormwater was evaluated. After the collection, each stormwater sample was analyzed for E. coli concentration. The cultured E. coli stock was added to the stormwater sample to achieve E. coli levels of 10^4 and 10^6 MPN/mL, respectively. The raw stormwater and the E. coli spiked samples were pumped through three steel chip columns under standard experimental conditions for 12 hours. Effluent samples were analyzed to determine E. coli removal efficiencies.

4.3 Analytical Methods

The pH was measured with an Orion 290A+ advanced ISE/pH/m/OPR meter (Therom Electron, Waltham, MA). The DOC concentrations were measured using a TOC-V CSH Analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310 B (APHA, 2012).

The approximate number of E. coli stock (cells/mL) was measured at UV 600 by a spectrophotometer (HACH DR/400 OU, Germany). The accurate value of E. coli concentration (MPN/mL) was quantified by the Colilert 18 (IDEXX) method. In the Colilert 18 (IDEXX) method, the water samples were added to 100 mL sterile vessels with one pack of Colilert reagent added to each. Sterile vessels were then capped and rotated until the Colilert reagent had dissolved. The sample/reagent mixtures were poured into Quanti-Tray /2000 and sealed by an IDEXX Quanti-Tray Sealer. All the sealed trays were then placed in a 35±0.5°C incubator for 24 hours and the results were read according to the Quanti-Tray/2000 MPN table provided by IDEXX.

For SEM analysis of steel chips, the samples were first washed with 0.01 phosphate buffered saline (136.75 mM NaCl, 0.27 mM KCl, 10.14 mM Na2HPO4, and 1.76 mM KH2PO4) and then added into 2.5% Glutaric dialdehyde solution (25% Glutaric dialdehyde mixed with 0.01 M PBS) for 24 hours to fix bacteria cells onto the steel chips' surface. Then samples were dehydrated with ethanol (30% - 100%). Last, samples were washed with liquid Tert-Butanol (TBA) and freeze-dried before the SEM test.

4.4 Results and Discussions

4.4.1 Effect of Different Operation Conditions on E. coli Removal

Figure 4.3 presents the effect of particle size, EBCT, influent concentration, and pH on E. coli removal by steel chip columns. It is evident that the E. coli removal efficiency gradually declined with the increasing size of steel chips. Steel chips in the size range of 0.5-1.0 mm showed the highest removal efficiencies. More than 99% of the influent E. coli was consistently removed by this column during the 72-hour operation. Steel chips in the largest size (4.0-8.0 mm) removed 95% of E. coli after a one-hour operation. After that, the E. coli removal efficiency gradually decreased and reached at 57% after a 12-hour operation. The E. coli removal by this steel chip column varied from 56.8% to 57.9% between the 12-hour and 72-hour operation. The E. coli removal performance of steel chips in the size ranges of 1.0-2.0 and 2.0-4.0 mm fell between the two above mentioned columns. The results were consistent with previous studies that showed smaller particles tend to have higher bacteria removal efficiencies (Kunkel et al., 2013; Mohanty and Boehm, 2014; Wu et al., 2019). The E. coli removal under standard experimental conditions (chips size =

1.0-2.0 mm, pH = 7.0, E. coli concentration = 10^6 MPN/mL, and EBCT = 10 min) varied between 89.5% and 99.2%.

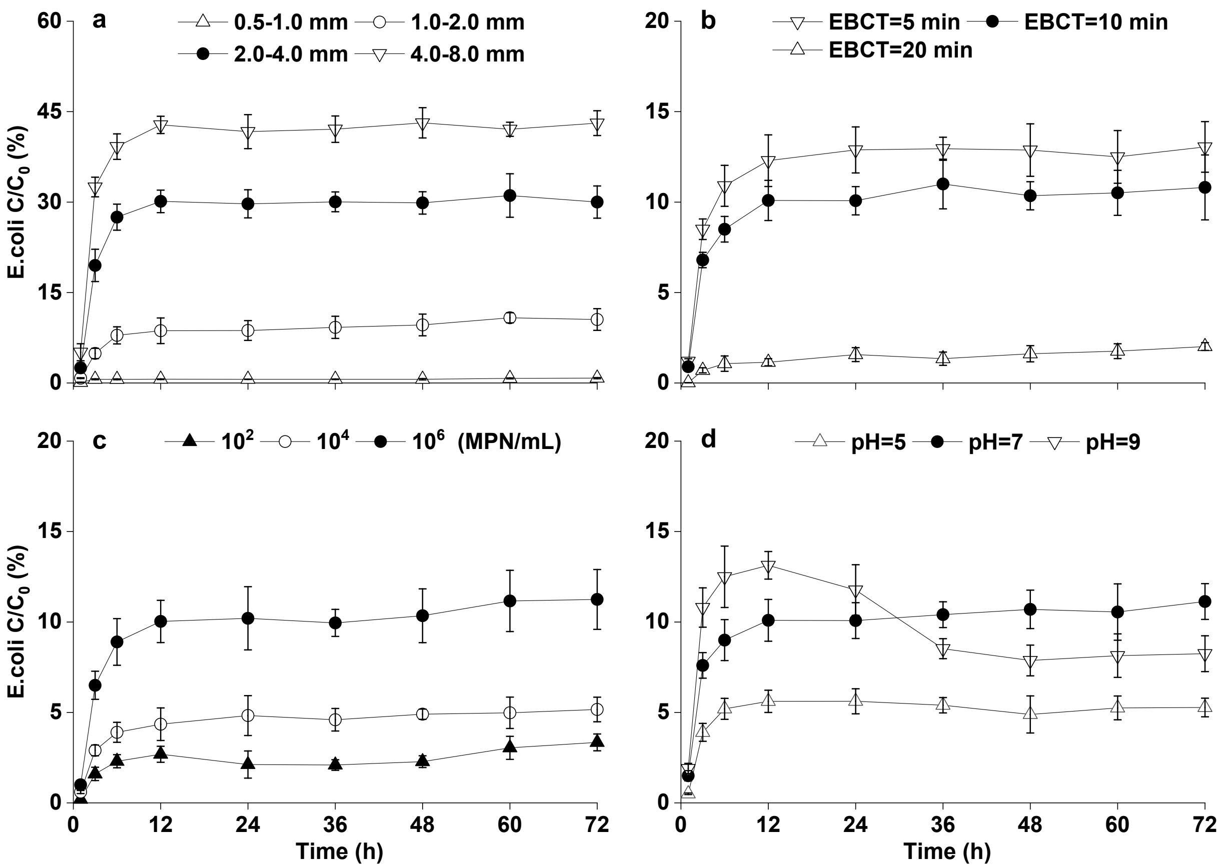

Figure 4.3 Effect of particle size, EBCT, influent concentration, and pH on E. coli removal

The U.S. EPA stormwater best management practice design guide recommends a minimum five-minute residence time for the stormwater filter (Environmental Protection Agency, 2004). As expected, the E. coli removal efficiency by steel chip columns decreased with increasing EBCTs. A longer EBCT leads to the longer exposure time of E. coli to steel chips and thus increases the E. coli removal. A similar impact of EBCT on biofiltration was also observed in previous studies (Hozalski, Bouwer, and Goel, 1999; Mohanty and Boehm, 2014; Liu et al., 2020). Nonetheless, the steel chip columns showed high E. coli removal for all three EBCTs. The average E. coli removal efficiencies were 87.2%, 89.5%, and 98.4% for 5-, 10-, and 20-minute EBCTs under stable operation conditions (12-72 h). To test the steel chip performance under different E. coli concentrations, the initial E. coli concentrations were varied from 10^2 to 10^6 MPN/mL. The effluent E. coli concentration increased with the increase of the initial E. coli concentration. However, the average E. coli removal only decreased by 9% as the influent E. coli concentration increased from 10^2 to 10^6 MPN/mL. This suggests that steel chip filters are able to maintain effective E. coli removal across a wide range of influent concentrations.

In general, steel chips performed better for E. coli removal under acidic environment. Many studies suggest the transport of bacteria within porous media is influenced by the surface electrostatic charge of the bacteria and the media materials (Bai and Lung, 2005; Jeng et al., 2005; Muirhead, Collins, and Bremer, 2006). E. coli exhibits negative charges in natural aquatic environments (Rijnaarts et al., 1995; Van Der Wal et al., 1997), whereas the steel chips have a positive charge. The opposite charges increase the attractive forces between E. coli and steel chips. The change of the solution pH will modify surface electrostatic charge of steel chips through ionization of iron oxides. The acidic environment will make the steel chips more positively charged, which can improve the E. coli attachment. This explains the general pH trends observed in this study. However, the E. coli removal at pH 9 showed a slightly different pattern. The removal efficiency was lower than that in pH 7 at the first 24 hours. After that, the E. coli removal steadily increased, and the removal efficiencies exceeded that at pH 7 between 36 and 72 hours. It is possible that the extended operation of steel chip columns under the pH 9 condition may have promoted the formation of ferric hydroxide, which is known to remove contaminants through coagulation in water treatment (Morgan and Lahav, 2007; Stumm and Lee, 2007). The existence of ferric hydroxide at pH 9 in this experiment was verified by visual examination of the column as reddish aggregates gradually accumulated on steel chips.

4.4.2 Effects of NOM on E. coli Adsorption and Detachment

NOM is ubiquitous in stormwater, and previous studies have reported that it can interfere with the removal of bacteria during stormwater treatment. Figure 4.4 presents the influence of NOM on the amount of E. coli attached to the steel chips. In the absence of NOM, the total attached E. coli was 0.23×10^8 MPN/g steel after six hours of operation. The attached E. coli linearly increased to 2.61×10^8 MPN/g steel after 72 hours. In the presence of 5 mg/L NOM, the quantities of attached E. coli were 0.18×10^8 MPN/g steel and 1.89×10^8 MPN/g steel, respectively, after six and 72 hours. These two values were 20.4% and 39.1% lower than the attached E. coli in the absence of NOM. When the NOM increased to 30 mg/L, the amounts of E. coli attached to steel chips were further decreased to 0.14×10^8 and 1.12×10^8 MPN/g steel after six and 72 hours of operation, representing 27.6% and 57.1% reductions compared with NOM free solution. These results demonstrate that the presence of NOM had a negative effect on the E. coli removal in steel chip filters. Similarly, Mohanty et al., (2013) found that the E. coli removal capacity of iron oxide-coated sand column decreased by 50% in the presence of 20 mg/L NOM after three hours of operation. Figure 4.4 also presents the quantities of NOM adsorbed onto the steel chips. The accumulative amounts of adsorbed NOM after 72 hours were 0.14 and 0.44 mg/g steel, respectively, in the presence of 5 and 30 mg/L NOM. The impact of NOM on E. coli adsorption can be explained by several mechanisms. First, the NOM can occupy the adsorption sites on the steel chip surface. Previous studies have shown that NOM is negatively charged and it can be adsorbed onto the iron oxide surface by ligand exchange (Chi and Amy, 2004; Foppen, Liem, and Schijven, 2008). Second, NOM can modify the surface charge of steel chips. Negatively charged NOM adsorbed onto the steel chip surface would decrease the surface charge, which will generate more repulsive electrostatic force between E. coli and steel chips, resulting in lower E. coli attachment (Chen et al., 2011).

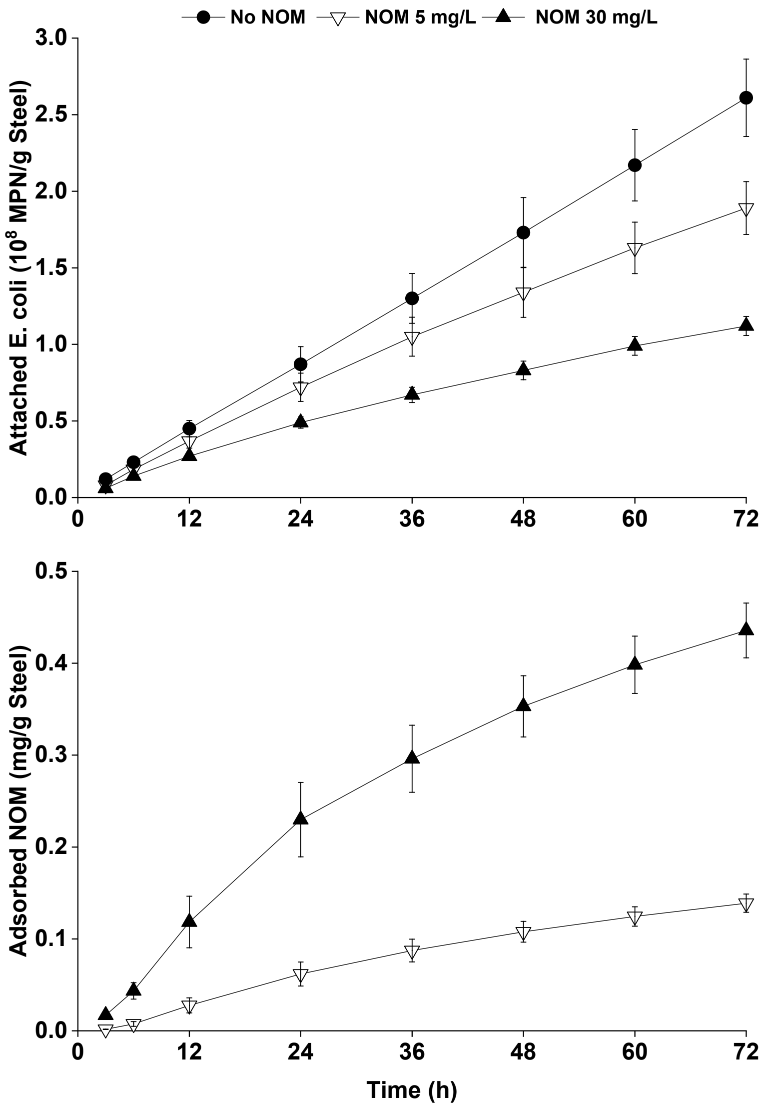

Figure 4.4 Effect of NOM on E. coli adsorption

The impact of NOM on E. coli detachment was also evaluated, and the results are shown in Figure 4.5. After flushing with one bed volume of solutions with different NOM levels, the E. coli concentrations in the effluents were 2.44×10^3, 8.50×10^3, and 11.32×10^3 MPN/mL for 0, 5, and 30 mg/L NOM, respectively. After a 12-hour flushing, the effluent E. coli concentrations decreased to 0.22×10^3, 4.50×10^3, and 5.80×10^3 MPN/mL, respectively. The accumulative amounts of detached E. coli accounted for 0.011%, 0.137%, and 0.175% of the initial E. coli attached to the steel chips before the flushing. These results showed that the NOM in the flushing water promoted E. coli detachment. However, the fractions of E. coli detached from steel chips under different NOM conditions were all very small. This suggests that a strong electrostatic attraction force existed between E. coli and steel chip surface and prevented the detachment of E. coli.

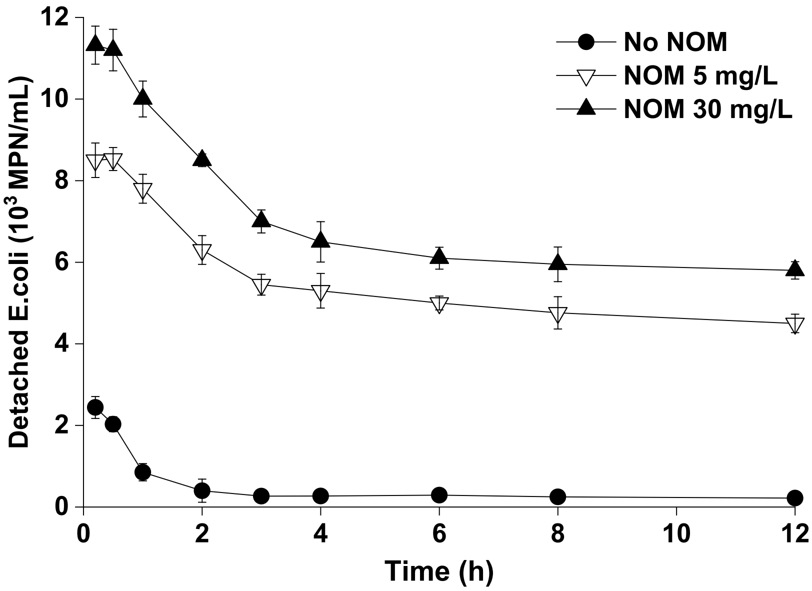

Figure 4.5 Effect of NOM on E. coli detachment

4.4.3 SEM Analysis

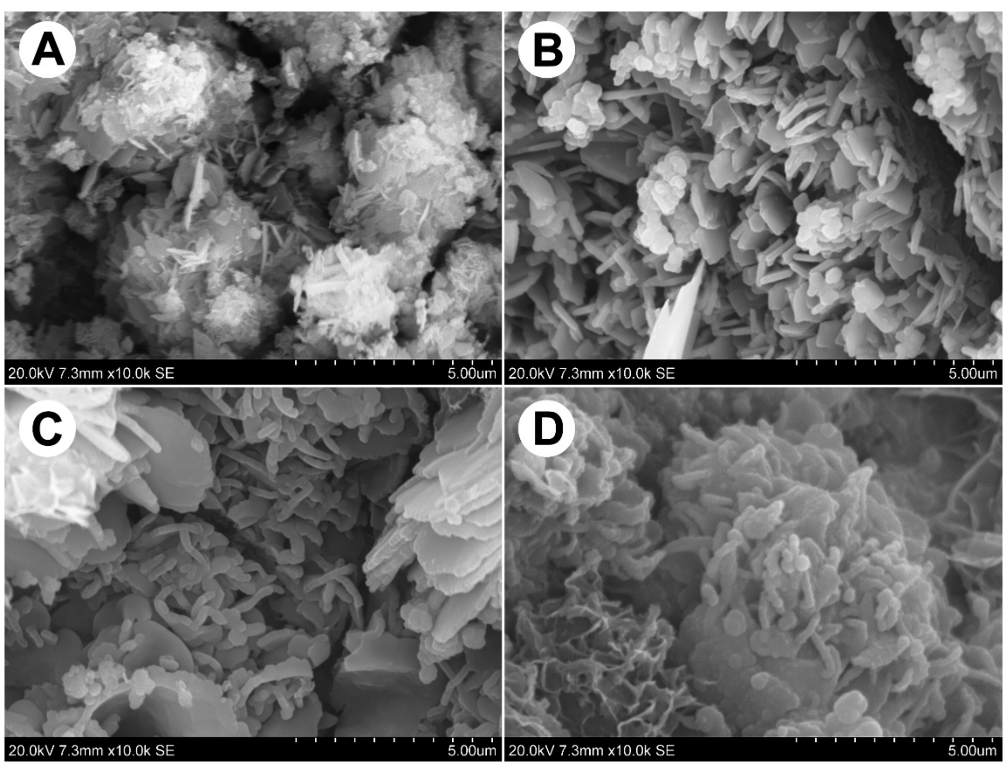

Figure 4.6 SEM images of steel chip surfaces (A: raw steel chip; B: E coli adsorption without NOM; C: NOM = 5mg/L; D: NOM = 30 mg/L.)

Figure 4.6 shows the SEM images of steel chip surfaces. The surface of raw steel chip (Image 3A) showed uneven characteristics and crystallization. The crystal that forms on the surface likely resulted from the formation of iron oxides. A high density of rod-shaped bacteria (E. coli) was observed on the surface of steel chip after the column experiment (Image 3B). This is the direct evidence for the E. coli attachment to the steel chips. In the presence of 5 and 30 mg/L NOM, the densities of attached E. coli generally declined as shown in Images 3C and 3D.

4.4.4 Effect of Intermittent Flow on E. coli Attachment

The E. coli removal during the short- and long-term intermittent flow conditions are shown in Figure 4.7. During the three cycles of short-term intermittent flow, the one-hour flow interval had little impact on the E. coli removal for the undrained steel chip column. The E. coli removal efficiencies varied between 87.5% and 90% after the restart of the flow for this column during the three cycles. A temporary increase of E. coli concentration (3-4 percentage points) was observed in the drained column after the one-hour interval time. However, the E. coli removal returned to typical conditions after 30 minutes of operation. The temporary increase of E. coli mobilization in the drained column can be explained by the air-water scouring when the flow restarted (DeNovio, Saiers and Ryan, 2004; Mohanty et al., 2013).

Similar to the short-term intermittent flow experiment, the long-term intermittent flow did not affect the E. coli removal in the undrained column. The E. coli removal remained relatively stable in this column during the three long-term cycles. However, a different pattern was observed for the drained column. After a 14-day flow interval, the drained column initially removed nearly all E. coli in the influent. The E. coli removal efficiencies gradually reached stable conditions after 12 hours. This E. coli removal curve is similar to that of a new steel chip filter. It was observed that the drained column was completely dry during the 14-day interval. It is expected that E. coli attached to the column would die off during the same period. Therefore, the E. coli of the drained column during the long-term intermittent flow would resemble a new steel chip filter. The intermittent flow experiments demonstrate that steel chip filters are able to maintain effective E. coli removal performance under short- and long-term intermittent flow conditions.

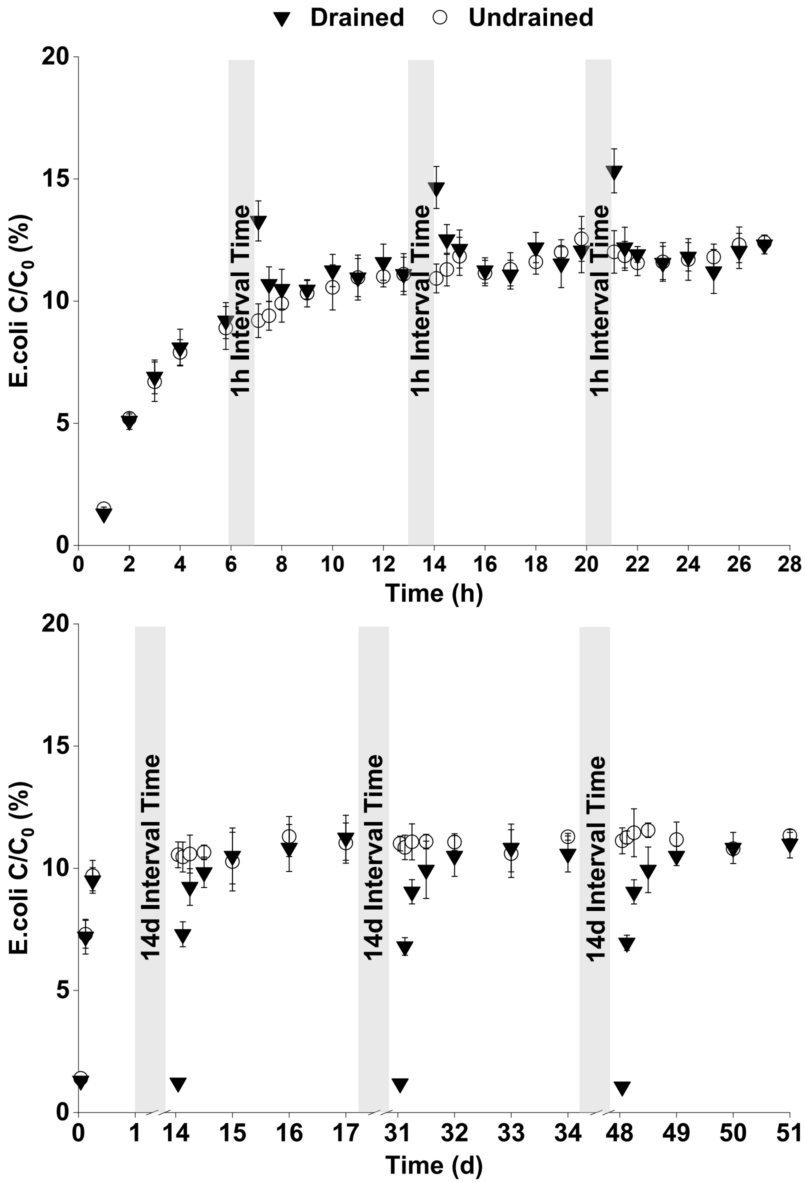

Figure 4.7 Effect of intermittent flows on E. coli removal by steel chip columns

4.4.5 The Steel Chips Performance in Real Stormwater

The E. coli removal efficiencies in real stormwater by the steel chip columns are presented in Figure 4.8. E. coli in both runoff waters were effectively removed by steel chips. The removal efficiencies were 91.3% to 99.6% and 89.7% to 99.4% for the stormwater collected from parking lot detention pond and residential detention pond, respectively, under ambient E. coli conditions. The slightly higher E. coli removal observed in the parking lot stormwater may be attributed to its relatively low DOC and TSS levels. When the E. coli levels in the real stormwater was spiked to 10^4 and 10^6 MPN/mL, the steel chip columns also achieved excellent E. coli removal efficiencies. This shows that steel chips are able to effectively remove E. coli present in real stormwater runoff.

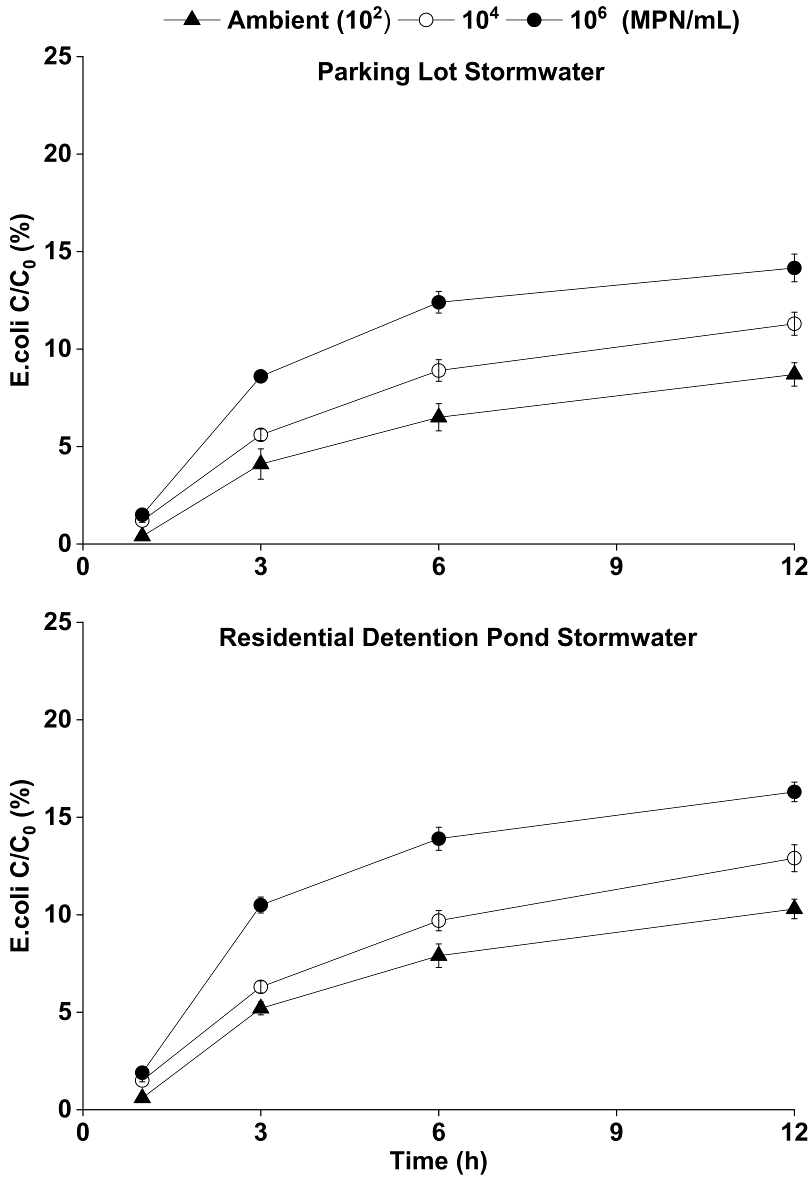

Figure 4.8 E. coli removal in real stormwater by steel chip columns

4.5 Conclusions

The goal of this project task was to evaluate E. coli removal in stormwater runoff by fixed-bed steel chip columns. The E. coli removal under standard experimental conditions (chips size = 1.0-2.0 mm, pH = 7.0, E. coli concentration = 10^6 MPN/mL, and EBCT = 10 min) varied between 89.5% and 99.2% during the 72-hour operation of steel chip columns. Smaller steel chip sizes, longer EBCT, lower initial E. coli levels, and lower pH values resulted in higher E. coli removal efficiencies in the steel chip columns.

The presence of NOM in water not only interfered with the E. coli removal but also affected E. coli detachment from steel chips. The accumulated quantities of E. coli removed by steel chips decreased by 39.1% and 57.1% after the 72-hour operation in the presence of 5 and 30 mg/L NOM. NOM also promoted the detachment of E. coli from steel chip surfaces during flushing. However, the detached E. coli only accounted for very small fractions of the initially attached E. coli before flushing.

Short-term intermittent flow temporarily decreased E. coli removal in the drained steel chip column, but the impact diminished quickly after the 30-minute operation. Short- and long-term intermittent flow did not affect E. coli removal in the undrained steel chip columns. Steel chip columns also effectively removed E. coli present in real stormwater runoff collected from parking lot and residential detention ponds. The results of the fixed-bed column experiments showed that steel chips are highly efficient materials for E. coli removal under continuous flow conditions. Field scale studies of steel chip filters are recommended to investigate their performance in real storm events.

5. FIELD-SCALE EVALUATION OF E. COLI REMOVAL FROM STORMWATER BY STEEL BYPRODUCTS

5.1 Introduction

Recycled steel chips demonstrated high E. coli removal capacities during the batch adsorption experiments. Steel slag also achieved good E. coli removal efficiencies. The results of fix-bed column experiments suggest that steel chip filters effectively removed E. coli under continuous flow conditions. It was determined that steel chips and steel slag should be further evaluated as filter materials under field stormwater events. The goal of this project task is to install a field-scale filter with steel chips and steel slag and evaluate the performance of this filter at different storm events. The project team identified a stormwater detention pond in a residential area in Brookings, SD, as the field stormwater filtration study site. A steel filter structure was installed at the inlet of the detention pond. Steel chips and steel slag were added to the filter structure and used as the filtration media. The removal of nitrogen, phosphorus, and E. coli by the mixed media filter was evaluated for different storm events.

5.2 Experimental Materials and Methods

5.2.1 Steel Byproducts

Recycled steel chips and steel slag were used as filter media in this study. Steel chips were collected from Alter Metal Recycling of Marshall, MN. The type of steel chips used for this experiment consisted exclusively of carbon steel chips. The steel slag used in this study was collected from Nucor Steel of Norfolk, NE.

Both materials were rinsed three times with deionized water to remove particles that may affect the adsorption process. They were also washed using phosphorus-free soap to remove oils that may be present on the surface of the steel byproducts. Once washed, the materials were air dried over 24 hours. The drying process allowed the steel chips to oxidize, producing a layer of rust over the material's surface. After the drying period, the materials were sieved into two size ranges using standard sieving procedures. The first range included small materials that were retained on a 2 mm sieve and passed through a 4 mm sieve. The second range included large materials that were retained on a 4 mm sieve and passed through a 9.4 mm sieve. An image of the two byproducts and their two size ranges can be seen in Figure 5.1. Once the materials had been sieved, they were subject to chemical and physical characterization tests following the American Society of Testing and Materials (ASTM) procedures. The packing densities of each material were found by finding the volume of a known mass of material while particle densities were found by displacing a known volume of water with a known mass of material. The pH of the materials was determined following ASTM D4972 and porosity was measured by taking a known volume of the materials and measuring the void space using water. The results from these tests can be found in Table 5.1.

Figure 5.1 Steel chips and steel slag used for field-scale filtration study (top: steel chips 2-4 mm and 4-9.4mm, bottom: steel slag 2-4 mm and 4-9.4 mm.)

Table 5.1 Characteristics of steel chips and steel slag used for field-scale filtration study

Material	**Size (mm)**	**Porosity (%)**	**Packing Density (g/cm^3)**	**Particle Density (g/cm^3)**	**pH**
Small Steel Slag	2-4	45.5	1.75	3.22	10.9
Large Steel Slag	4-9.4	52	1.36	2.83	10.9
Small Steel Chips	2-4	75	1.32	5.3	6.3
Large Steel Chips	4-9.4	80.5	0.83	4.96	6.3

5.2.2 Batch Adsorption

Batch adsorption experiments were conducted to compare E. coli removal by the selected steel byproduct materials before the field study. The experiments tested the materials against different E. coli concentrations and contact times to acquire a better understanding of how the materials will perform under field scale conditions.

One gram of steel slag and chips were used for comparing the removal efficiency of the materials at different E. coli concentrations of 10, 100, 1,000, and 10,000 MPN/mL. These concentrations were acquired through diluting the cultured E. coli to the required MPN/mL. Four different materials were tested for each E. coli concentration: small slag, large slag, small chips, and large chips. The material masses were measured and put into separate Erlenmeyer flasks that were filled with 100 mL of corresponding E. coli solution. The flasks were shaken continuously at 100 rpm with an orbital shaker for two hours at a constant temperature of 20˚C. After the two-hour duration, the samples were removed from the orbital shaker and analyzed using the IDEXX Quanti-Tray/2000 method.

An adsorption kinetic experiment was also conducted to quantify the rate in which E. coli absorbs to the surface of steel byproducts. To provide a better understanding of how the materials will work under real world conditions, short sampling intervals were used. One gram of each material and an E. coli concentration of 100 MPN/mL were used for the kinetic experiment. This concentration was determined using the general batch test results along with the concentration reflecting E. coli concentrations that may be found in urban stormwater runoff. The samples were shaken at 100 rpm with an orbital shaker at a constant temperature of 20 ˚C with contact times of 5, 15, 30, 60, and 120 minutes. The samples were analyzed using the IDDEX Quanti-Tray/2000 method. The adsorption data were fitted to first and second order rate equations. The linear form of first order rate equation is as follows.

$$\ln[A] = \ln[A]_0 - kt \qquad \text{(Equation 5.1)}$$

Where [A] is the concentration of E. coli at time t (MPN/mL), $[A]_0$ is the initial concentration of E. coli (MPN/mL), k is the rate constant, and t is time (min).

The second order rate equation can be seen as follows.

$$\frac{1}{[A]} = \frac{1}{[A]_0} - kt \qquad \text{(Equation 5.2)}$$

5.2.3 Field Scale Filtration Site Conditions

The field scale filter was installed at the inlet to a retention pond located near the corner of Camelot Drive and Breckenridge Lane in Brookings, SD. A satellite image from Google Maps of the site can be seen in Figure 5.2. Figure 5.3 shows a stormCAD image of the catchments and Storm Sewer Layout provided by the City of Brookings Engineering Office and created by Banner Associates, Inc. Geological information on the site was provided by the City of Brookings Engineering Office through a land survey that was performed by Banner Associates, Inc. Information from this survey can be found in Table 5.2. The retention pond is located downstream of a 16.16-acre drainage basin. This basin for design purposes is split into nine different sub-catchments whose runoff is delivered to the retention pond through a 2-ft diameter pipe ending with a 4-ft end wall culvert.

Figure 5.2 Satellite image of field–scale filtration site location taken from Google Maps

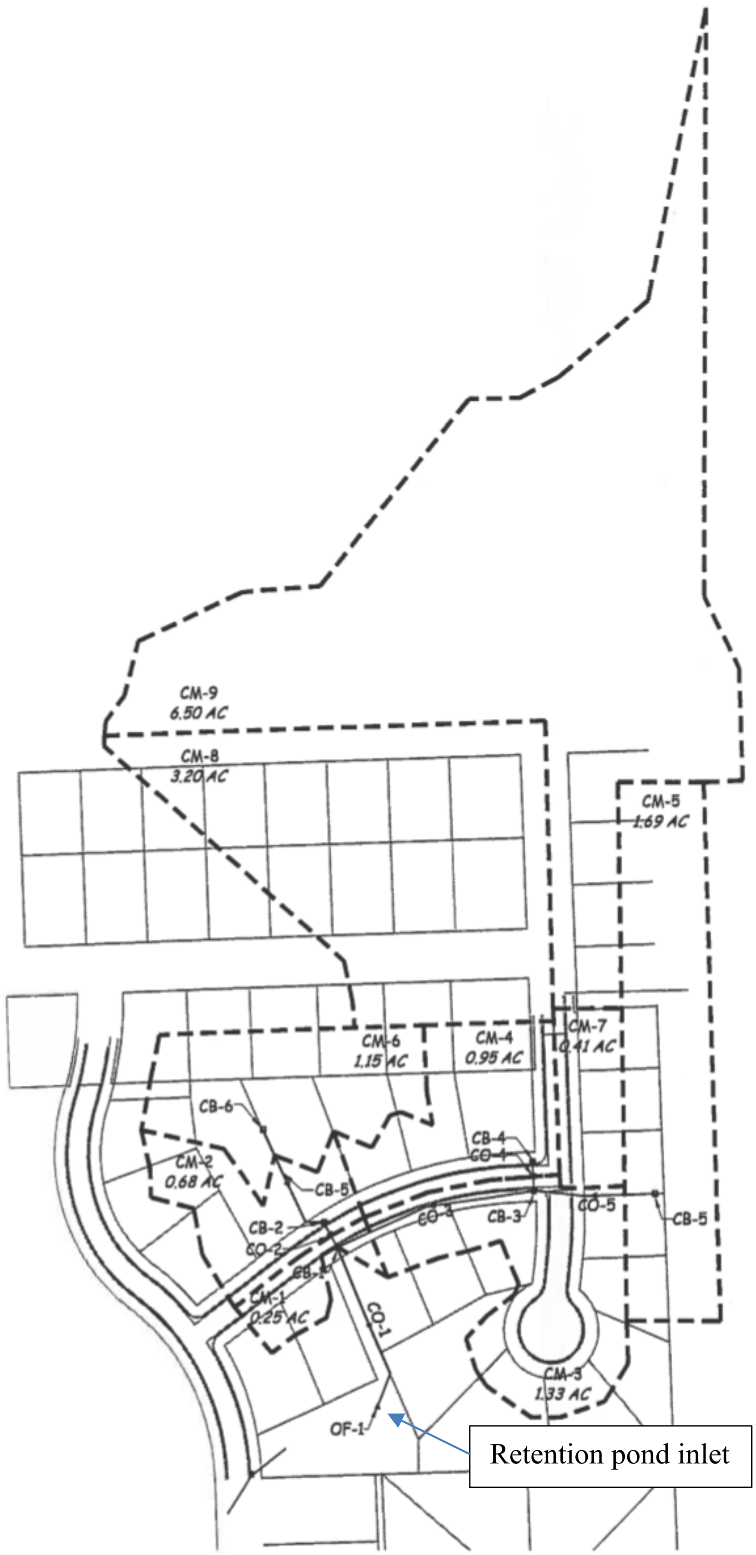

Figure 5.3 StormCAD catchments and storm sewer layout of the drainage area of the study site

Table 5.2 Field filtration study site drainage conditions

	Catchments								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Area (Acres)	0.25	0.68	1.33	0.95	1.69	1.15	0.41	3.2	6.5
Percent Impervious (%)	40	40	40	40	40	40	40	40	40
Soil Type	C	C	C	C	C	C	C	B	B

5.2.4 Field Scale Steel Byproduct Filter Design

The filter was designed to fit the retention pond inlet. The filter's dimensions were designed to be 5 ft wide, 6 ft long with an 8 in height. The inlet and outlet plates of the structure had 1 in. diameter holes drilled into them to let runoff pass through the filter creating a free-flowing structure. A schematic of the plates used to create the filter structure can be seen in Figure 5.4. The structure was fabricated entirely by Bend Rite Custom Fabrication Inc. and was made out of A36 ¼ in. mild steel. The mixed media chosen for this filter was made up of 25% large steel slag, 12.5% small steel slag, 50% large steel chips, and 12.5% small steel chips. The ratios of size and byproduct type were selected using the batch test results and knowledge over the material's properties. Steel chips are known to agglomerate over time, which could clog the filter and reduce the amount of treated runoff. The higher percentage of large steel slag and large steel ships used over their smaller counterparts was done to counteract this agglomerating effect and increase the lifespan of the media. Figure 5.5 shows the processed media to be used in the filter along with oversized slag that was retained on a 9.4 mm sieve. The filter was filled to a depth of 6 in. with the mixed media to allow 2 in. of free board. A layer of oversized slag was placed in front of the structure to remove debris that could clog or harm the filter.

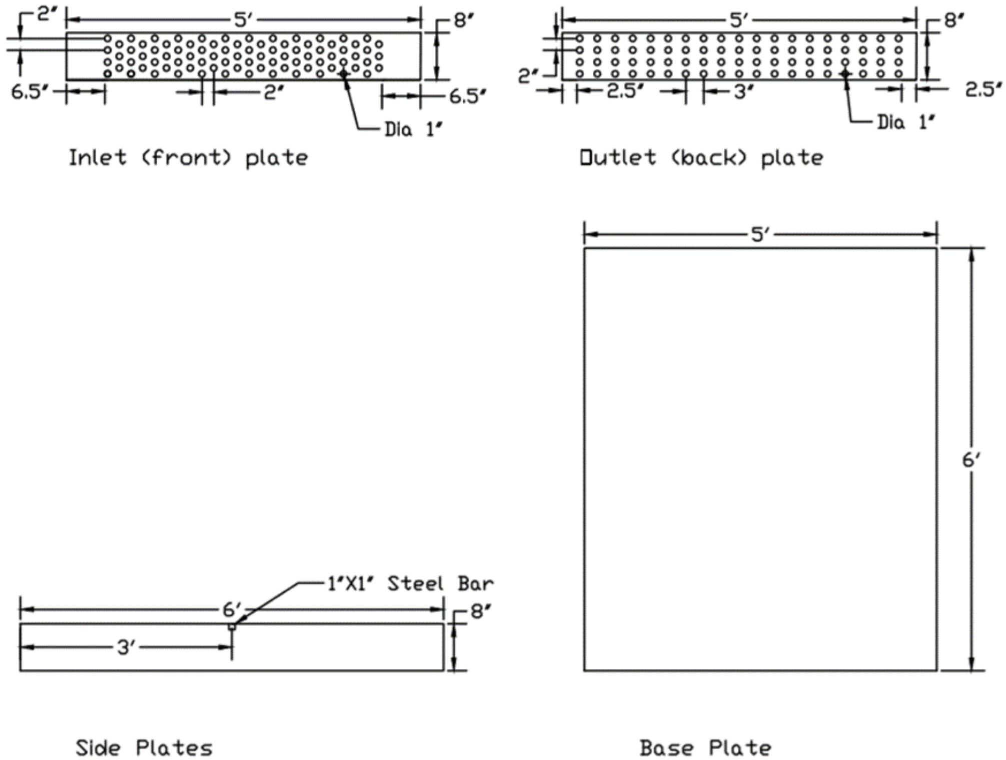

Figure 5.4 Schematic of plates used to create the field scale filter

Figure 5.5 Filter media prepared for field-scale stormwater filtration study

Figure 5.6 shows the filter on-site during a runoff event. Influent and effluent samples were collected during storm events to evaluate the performance of the mixed media filter.

Figure 5.6 Field scale stormwater filter installed at a residential stormwater detention pond.

5.2.5 Field Scale Filter Maintenance

After the first month of the filters' usage, it was found that the rusting iron media were agglomerating. This would occur after a rain event once the media had dried. To prevent this from occurring between rain events, once the filter was dried, the media were broken up with a pickaxe to get the filter ready for the next runoff event.

5.2.6 Sampling Method

Four storm events were sampled during the three-month testing period (July to September 2018). These four events occurred in 2018 on 7/12, 8/19, 8/27, and 9/17 Filter influent and effluent grab samples were taken simultaneously every 15 minutes during a runoff event. Samples were never taken during overflow events in which the effluent water level surpassed the 6 in. media depth. Samples were stored in a cool, dark, and dry place during the sampling process and were immediately transported to South Dakota State University's environmental laboratory upon the completion of the runoff event. Temperature was recorded on-site immediately after samples were taken along with flow rate. Flow rate was measured at the stormwater channel before the filter using the cross-sectional method. The equation used for calculating the flowrate is as follows.

$$R = \frac{WDaL}{T} \quad \text{(Equation 5.3)}$$

Where "R" is rate of flow (cfs), "W" is the average width (ft.), "D" is the average depth (ft.), "L" is the average length (ft.), "T" is the time for a float to traverse the length (sec), and "a" is the constant for the correction of stream velocity. The length used was a short distance inside the stormwater channel in front of the filter. To find the time a float takes to traverse the length, a rubber ball floating the length was timed with a stopwatch. A value of 0.9 was used for the correction constant since the bottom of the channel is composed of concrete and assumed to be smooth. The flowrates of the runoff events at time of sampling can be found in Table 5.3. Storm-specific data such as precipitation start time, runoff temperature, and total precipitation can be found in Table 5.4. Precipitation start time and temperature were all recorded on-site while total precipitation was taken from South Dakota State University's Mesonet database.

Table 5.3 Flow rates measured at time of sampling during the storm events

Time (min)	12-Jul	19-Aug	27-Aug	17-Sep
0	0.38	0.38	0.82	0.35
15	0.39	0.34	0.56	0.42
30	0.44	0.32	0.42	0.44
45	0.36	0.36	0.67	0.23
60	0.32	0.41	0.78	0.21
75	0.36	0.36	0.35	0.21
90	0.36	0.23	0.26	0.36
105	0.30	0.41	0.23	0.27
120	0.24	0.30	0.19	0.24
135	0.21			0.27
150				0.36
165				0.26

Table 5.4 Precipitation conditions for the four runoff events

	Runoff Events			
	7/12/2018	**8/19/2018**	**8/27/2018**	**9/17/2018**
Precipitation Start Time	7:15 PM	1:30 PM	9:00 AM	12:15 PM
Temp (˚F)	70	71	71	66
Total Precipitation (in.)	0.79	0.57	0.41	1.04

The filter hydraulic retention time was calculated using the equation shown below.

$$t = \frac{V*n}{Q} \quad \text{(Equation 5.4)}$$

Where "t" is the retention time (sec), "V" is the volume of the structure (ft^3), "n" is porosity and "Q" is the flow rate. Due to the structure being mixed media, the porosity used in the calculation was a weighted average of 68.3%. Table 5.5 presents the hydraulic retention times (HRT) determined during the stormwater event. The HRTs varied from 13 to 53 seconds. In general, the filter performance determined through this field study was obtained under relatively short retention times.

Table 5.5 Hydraulic retention times of the filter during storm events

Time (min)	12-Jul	19-Aug	27-Aug	17-Sep
0	27	27	13	29
15	26	30	18	24
30	23	32	24	23
45	28	28	15	45
60	32	25	13	48
75	28	28	29	50
90	28	45	39	28
105	34	25	45	37
120	43	34	53	43
135	48			38
150				28
165				39

5.2.7 Analytical Methods

Upon the samples arriving at the environmental laboratory, the pH of samples was immediately measured using an Orion 290 A+ advanced ISE/pH/mV/ORP meter (Thermo Electron Corporation, Waltham, MA.). The probe was calibrated using 4, 7, and 10 buffers. Once the pH was measured, the IDEXX test was performed to measure the E. coli concentration of the samples. The pH and IDEXX tests were always performed on the same day the samples were taken.

Water quality parameters, including total phosphorus, dissolved orthophosphate, dissolved nitrate, and dissolved iron, were also measured. These tests were performed using colorimetric methods where dissolved orthophosphate was measured as mg/L of PO_4^{3-}, dissolved nitrate as mg/L of NO_3-N, total phosphorus as mg/L of PO_4^{3-}, total nitrogen as mg/L of N, and dissolved iron as mg/L of Fe. These parameters were analyzed using a DR/4000U Spectrophotometer (HACH, Loveland, Co.). For dissolved orthophosphate, nitrate, and iron tests the samples were filtered using 0.45-micron pore size filters before being measured with their corresponding colorimetric methods. Tests were all ran within 48 hours of sampling, and samples were kept refrigerated during their holding time.

5.3 Results and Discussion

5.3.1 Batch Study Results

The results of the general batch study can be found in Figure 5.7. The figure shows how differential initial E. coli concentrations affect the performance of steel chips and slag of two different size ranges. The results illustrate that with an increase in E. coli concentration there is a decrease in removal efficiencies. Large steel slag only removed 28% of the 10 MPN/mL E. coli concentration and no apparent removal was observed when the concentration increased to 100, 1,000, and 10,000 MPN/mL. The other three materials—small slag, large chips, and small chips—showed 23% to 60%, 72% to 82%, and 89% to 95% removal percentages, respectively. Steel chips were minimally affected by differences in E. coli concentrations, whereas the steel slag's removal capacity was reduced by more than half when increasing E. coli from 10 to 10,000 MPN/mL.

Steel chips showed much higher E. coli removal efficiencies than steel slag, which is consistent with previous laboratory batch adsorption experiments.

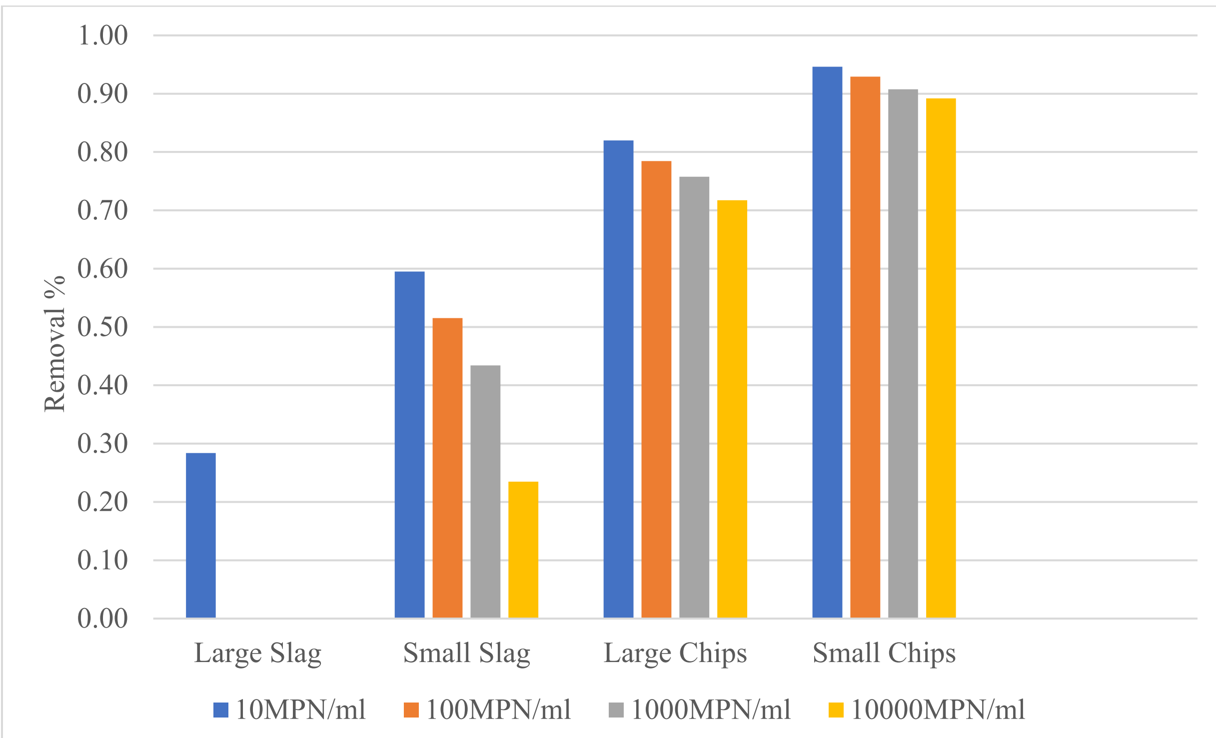

Figure 5.7 Effect of initial concentrations on E. coli removal by filter materials

5.3.2 Adsorption Kinetics

Figure 5.8 shows the rate in which E. coli adsorbs to each of the four materials. Large steel slag did not show apparent E. coli removal over the two-hour time span. Small and large steel chips showed fast E. coli removal rates. Within the first five minutes, the large chips and small chips, respectively, removed 15% and 21% of the initial E. coli concentration. The removal percentages quickly rose to 75.6% and 86.8% for the two steel chips after 60 minutes, then gradually reached 82.4% and 93.0% after 120 minutes for the two steel chips. Small steel slag showed more gradual increases in E. coli removal during the kinetic experiment and reached 48.6% removal after two hours.

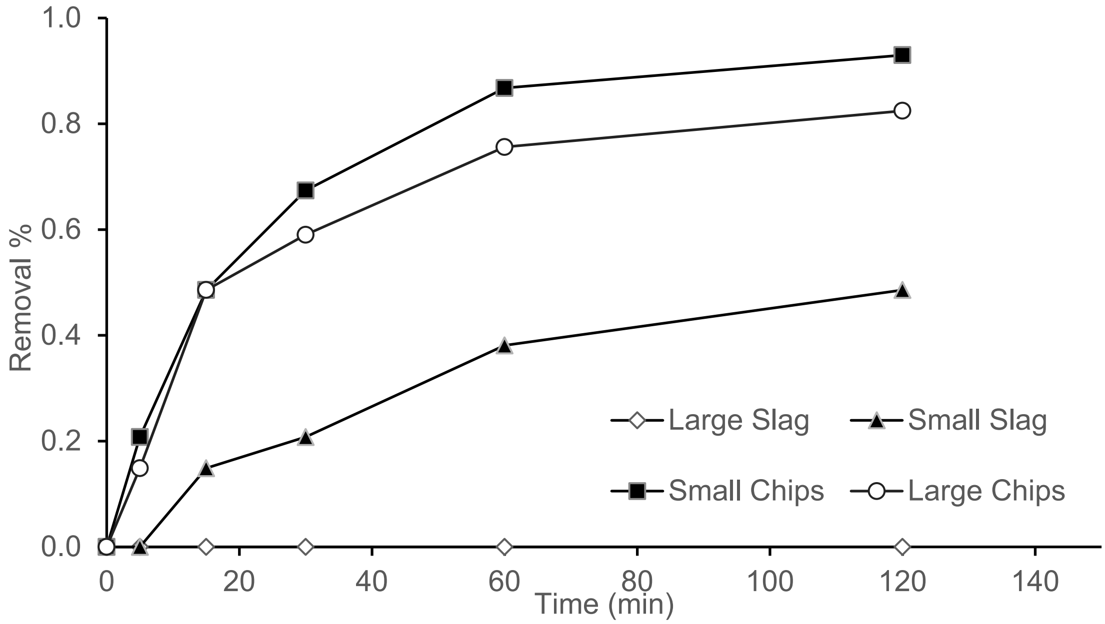

Figure 5.8 E. coli removal at different times by filter materials

The results for the three materials that removed E. coli were also fitted to both first- and second-order rate equations. Table 5.6 shows modeling results. Overall, second-order kinetics fit the E. coli removal data better than the first-order kinetics as evidenced by the higher coefficients (R^2).

Table 5.6 Kinetic model parameters for E. coli removal by filter materials

Material	Size (mm)	First Order		Second Order	
		$K_1(h^{-1})$	R^2	K_2(ml/MPN-h)	R^2
Small Slag	2-4	0.34	0.94	0.004	0.97
Large Slag	4-9.4	-	-	-	-
Small Chips	2-4	1.33	0.93	0.048	0.99
Large Chips	4-9.4	0.84	0.87	0.018	0.97

5.3.3 Field Scale Filtration Results

5.3.3.1 E. coli Removal

Figure 5.9 shows influent and effluent E. coli concentrations versus time for the four storm events (7/12, 8/19, 8/27, and 9/17) during the field filtration study. It was found that the influent E. coli varied substantially during each storm event. The E. coli concentrations received by the filter ranged from 5.2 MPN/mL to 261.3 MPN/mL. The mixed media filter was able to remove averages of 55%, 54%, 43%, and 49% of E. coli for the four stormwater events, respectively. The steel chips and steel slag mixed media filter achieved an average of 50% removal of E. coli during the field scale study.

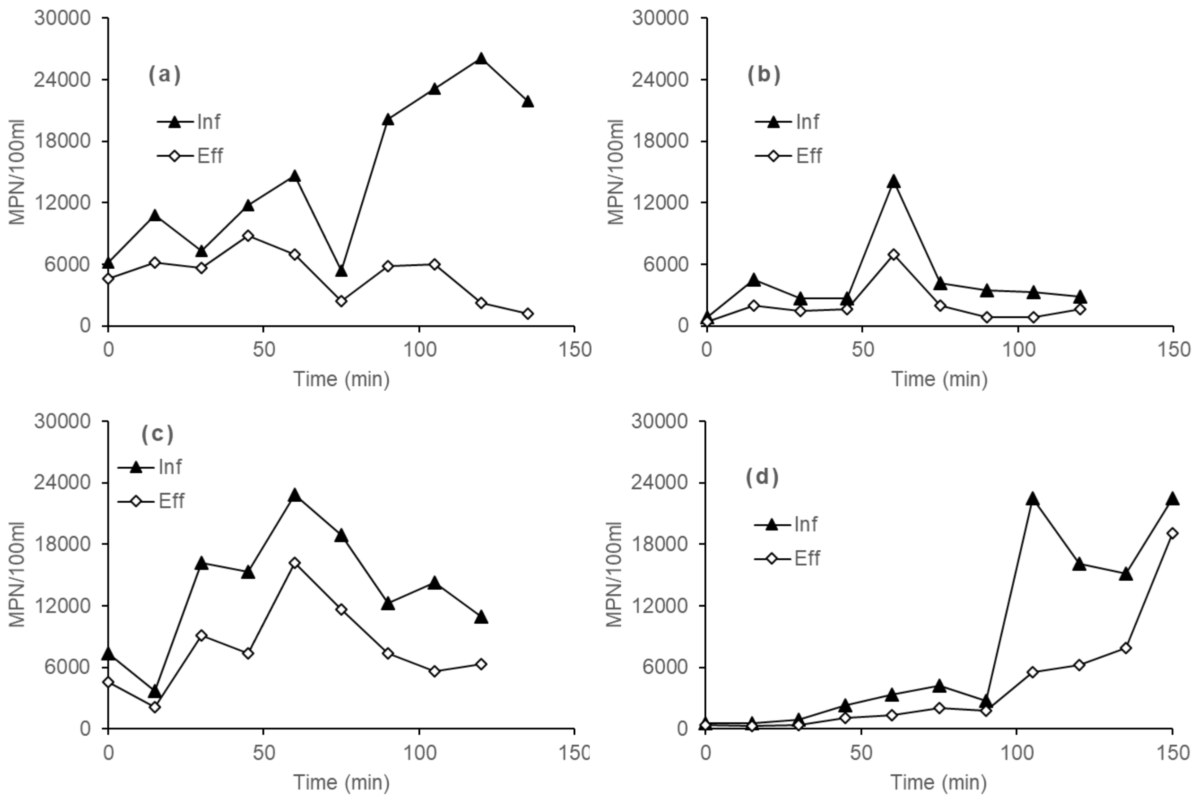

Figure 5.9 E. coli removal by field scale filter during the four storm events

The E. coli removal efficiencies by the mixed media filter were lower than that obtained during the batch adsorption experiment. This can be attributed to the much shorter retention time and the mixed media design for the field filter. Nonetheless, the field study results suggest that steel chips and steel slag media filtration is an effective technology for E. coli removal from stormwater runoff.

The E. coli removal efficiencies by the mixed media over this three-month study period did not show many variations among the four storm events. This indicates that the field filter was able to maintain its E. coli removal capacity during the three months. It is possible that steel chips in the filter were continuously oxidized, thereby creating new adsorption sites for E. coli removal over time.

5.3.3.2 Phosphorus Removal

Figure 5.10 shows the total phosphorus percent removals for the four runoff events. The mixed media filter removed averages of 37%, 30%, 24%, and 26% of total phosphorus during the four storm events. The average percent removal over the four events was 29%. The total phosphorus concentrations in the stormwater before the filter ranged from 0.63 mg/L to 2.06 mg/L. Fertilizers used for lawns in the drainage area may be the major source of this nutrient.

Orthophosphate is a soluble reactive phosphorous and the most bioavailable form of phosphorus. Figure 5.11 presents the removal of dissolved orthophosphate for the four runoff events. The dissolved orthophosphate concentrations received by the filter ranged from 0.12 mg/L to 0.90 mg/L. After the mixed media filter, averages of 32%, 49%, 36%, and 50% of dissolved orthophosphate were removed during the four storm events. The overall average percent removal over the four events was 42%. Steel slag and steel chips are rich in metal oxides species, including iron, aluminum, and calcium. These metal oxides can remove phosphate through electrostatic adsorption, ligand exchange, and precipitation. The results in

Figures 5.10 and 5.11 demonstrate that a steel chip and steel slag mixed media filter is also capable of phosphorus removal under field stormwater conditions.

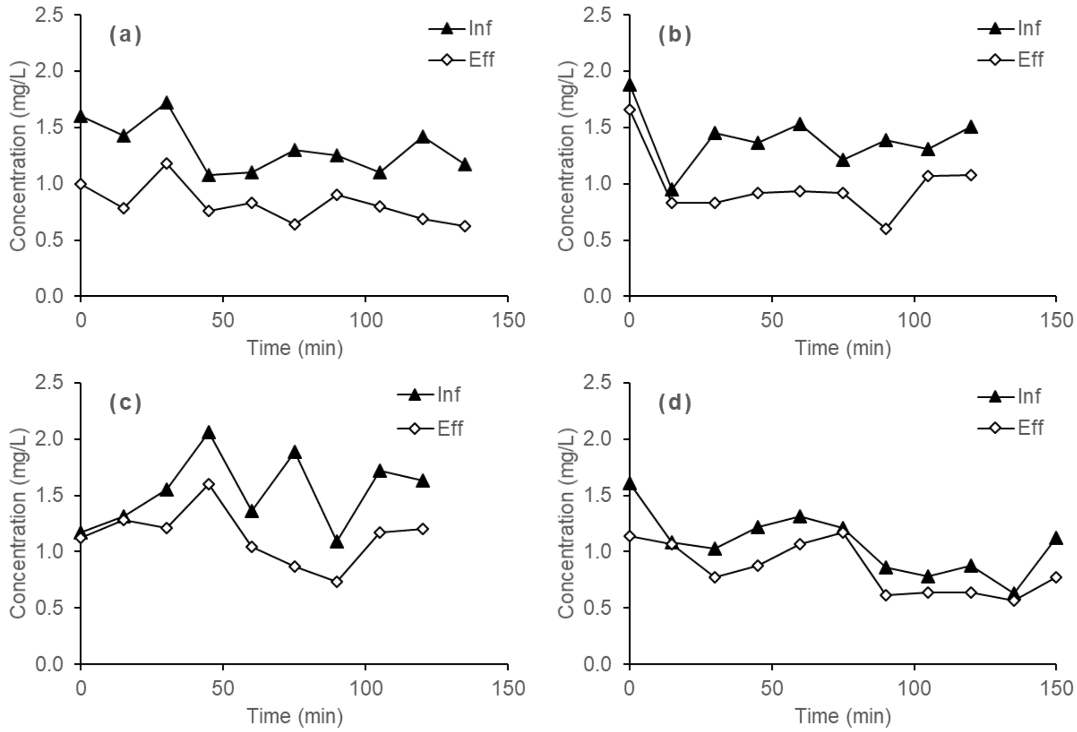

Figure 5.10 Total phosphorus removal by field scale filter during the four storm events

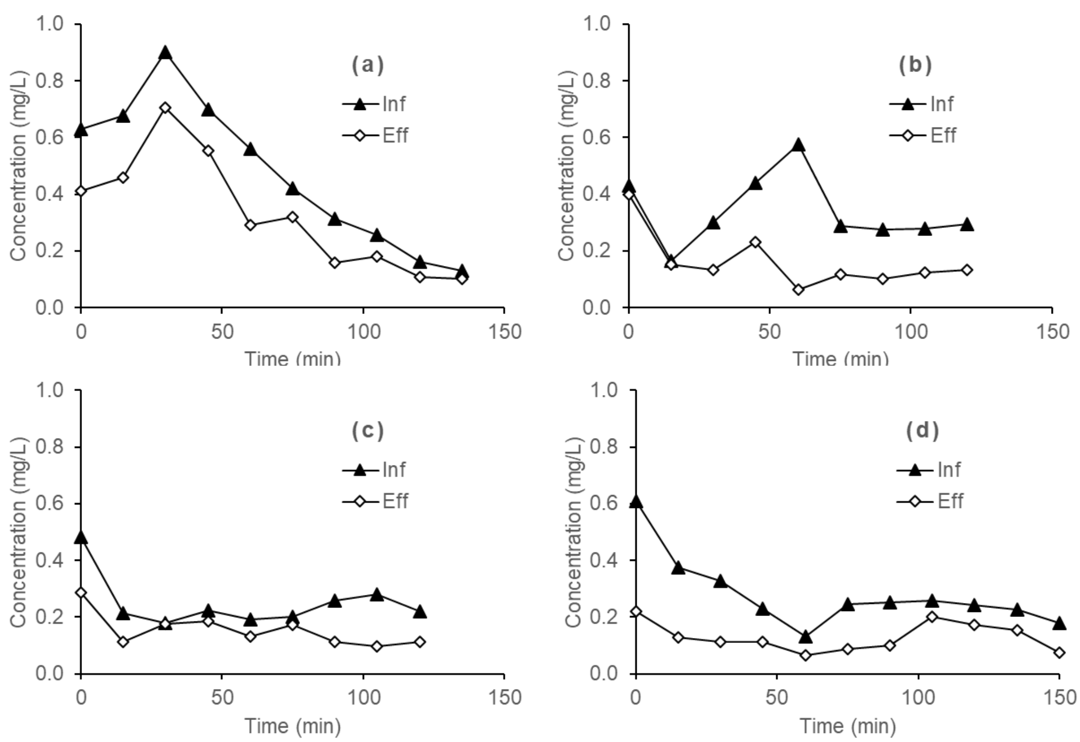

Figure 5.11 Orthophosphate removal by field scale filter during the four storm events

5.3.3.3 Nitrate Removal

Figure 5.12 shows the variations of dissolved nitrate in the influent and effluent of the filter for each runoff event. The influent nitrate concentrations varied from 0.6 to 1.9 mg/L with an average of 1.17 mg/L. The only indication of dissolved nitrate removal by the filter was observed for several sampling points during the first storm events (part (a) of Figure 4.11). The removal ranged from 7% to 23%. However, the mixed media filter did not show appreciable nitrate removal for the other three storm events. This suggests that steel chips and steel slag are not effective materials for nitrate removal from stormwater.

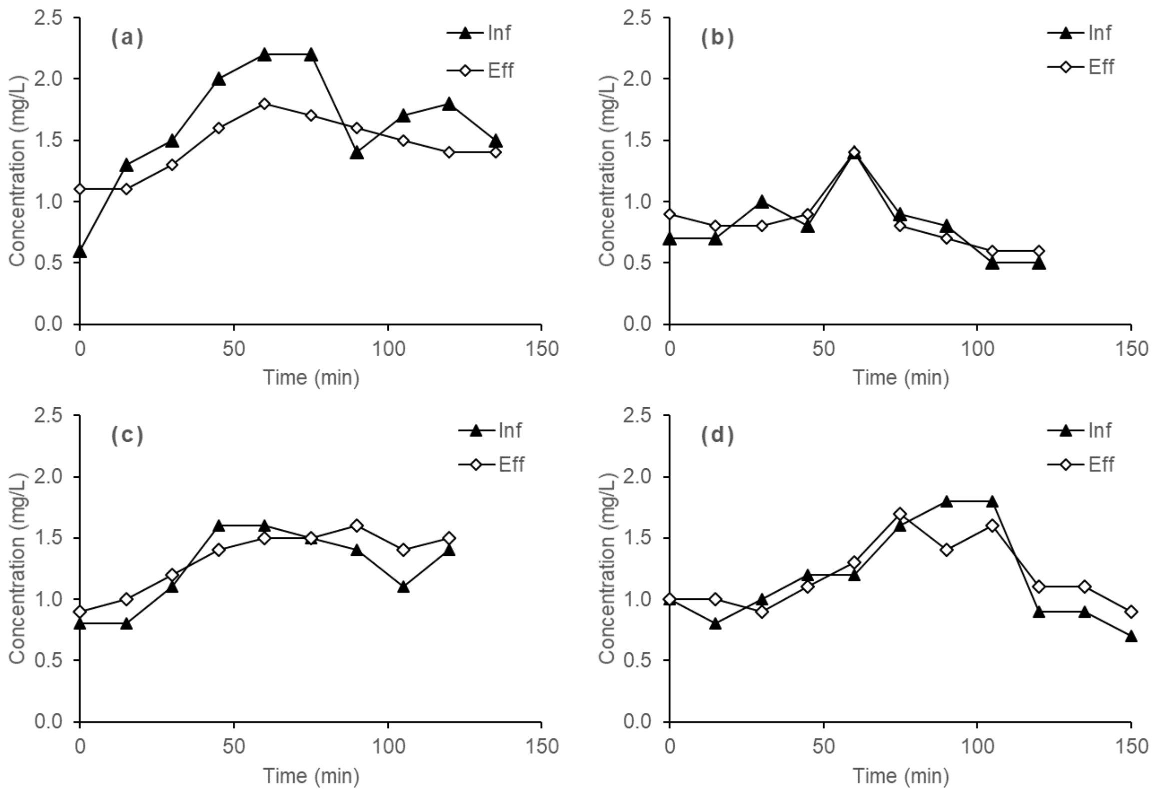

Figure 5.12 Nitrate removal by field scale filter during the four storm events

5.3.3.4 Effect of filter media on effluent pH and dissolved iron

The pH values of the filter influent and effluent samples were monitored for each storm event, and the results are presented in Figure 5.13. Throughout the four runoff events the effluent was found to consistently have higher pH values than that of the influent. The average influent pH over the four runoff events was found to be 6.8 while the effluent was found to be 8.2. The filter media increased the pH value of the stormwater by an average of 1.4. The cause of this increase in pH is due to the steel slag being alkaline with a pH of 10.9. Similar pH impact by steel slag during water treatment was also reported previously (Penn et al., 2012).

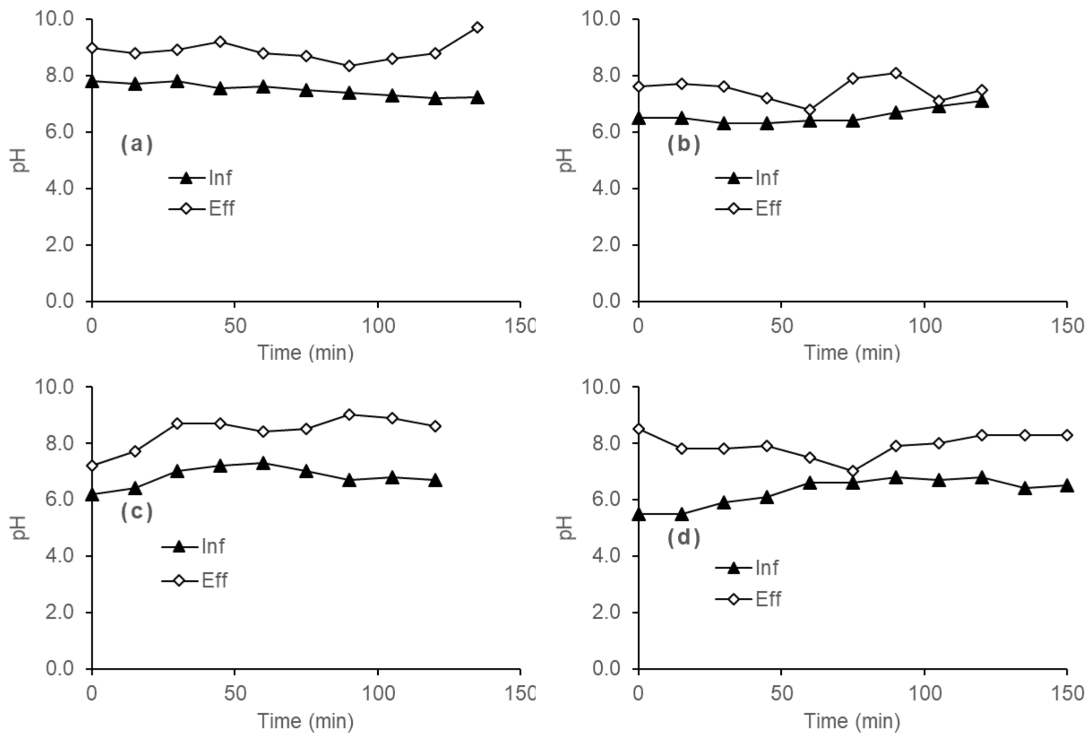

Figure 5.13 Effect of filter media on pH of treated effluents

The effect of the filter media on dissolved iron concentrations in treated effluent was examined throughout the four runoff events. Figure 5.14 shows the influent and effluent concentrations of dissolved iron for each runoff event. It can be seen that dissolved iron concentrations generally increased after the stormwater treatment by the filter media. This is expected because of the use of steel byproducts in the filter. The average influent iron concentration over this study period was 0.17 mg/L. The iron released from steel media increased the dissolved iron to an average of 0.67 mg/L in the effluents.

The EPA's drinking water regulations have a secondary standard for iron of 0.3 mg/L (EPA 2009). The effluent dissolved iron concentration for this pilot scale test exceeded this secondary standard on 25 of the 40 samples tested. Therefore, a post-treatment may be necessary to reduce iron concentrations when the effluent is discharged to sensitive water bodies.

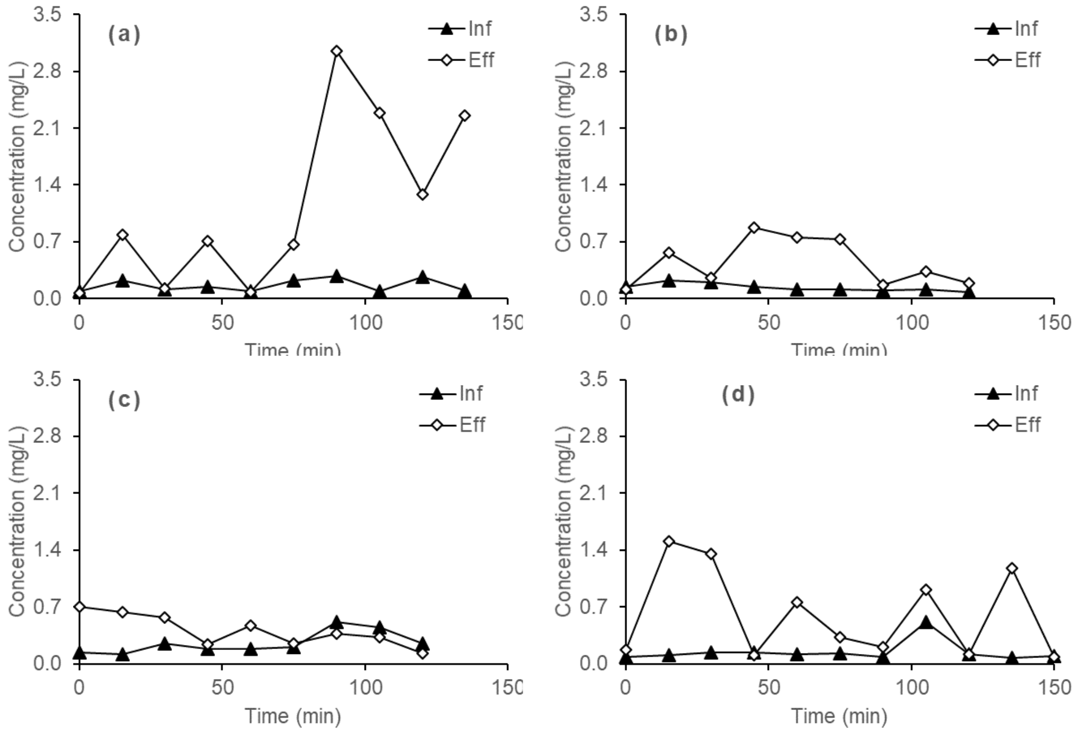

Figure 5.14 Effect of filter media on dissolved iron in treated effluents

5.4 Conclusions

The objective of this project task was to investigate the removal of E. coli and other contaminants from stormwater using mixed media filtration under field stormwater runoff conditions. The mixed media are comprised of recycled steel chips and steel slag. Laboratory batch experiments were first conducted on the two materials to determine their E. coli removal efficiencies under controlled laboratory conditions. The two materials were separated into two size ranges, small particles (2-4 mm) and large particles (4-9.4 mm). A batch study compared E. coli removal from steel chips and steel slag after two-hour adsorption for different initial concentrations of 10, 100, 1,000, and 10,000 MPN/mL. A kinetic study was also conducted to determine the E. coli removal rate of different materials.

The results of the laboratory batch study showed that smaller filter materials removed more E. coli than larger materials and that steel chips were much more effective at E. coli removal than steel slag. The E. coli removal efficiencies of steel chips were not largely affected by the initial concentration. The steel chips also exhibited faster E. coli removal kinetics than steel slag.

A stormwater detention pond in a residential area of Brookings, SD, was selected as the field study site to evaluate the performance of mixed media filtration for stormwater treatment. The filter structure is 6 feet long by 5 feet wide by 8 inches high and was placed at the inlet of the detention pond. The filter was filled with the mixed media to 6 inches high; the filter media were comprised of 25% large steel slag, 12.5% small steel slag, 50% large steel chips, and 12.5% small steel chips. Four storm events between July and September 2018 were monitored to determine the treatment efficiencies of the filter. The results showed that the mixed media removed an average of 50% of the E. coli and an average of 42% of phosphate in the runoff under the hydraulic retention times of 23-50 seconds. The mixed media maintained stable E. coli and phosphate removal efficiencies throughout the field experiment. These results demonstrate that mixed media filtration using recycled steel chips and steel slag is an effective technology for removing E. coli and phosphate from stormwater under field conditions.

6. SUMMARY AND RECOMMENDATIONS

6.1 Research Summary

Stormwater runoff has been recognized as a major source of water contaminants that can deteriorate the surface water quality. Contaminants carried by stormwater present a serious risk to aquatic ecosystems and public health. As we continue to expand urbanization and agricultural production, contamination caused by stormwater is likely to worsen in the future. Therefore, effective treatment technologies are needed to improve stormwater management and protect natural water resources. Media filtration is a promising technology for removing multiple contaminants from stormwater. Most previous studies on stormwater filtration focused on particles, nutrients, and heavy metals in laboratory scale experiments. Few studies have evaluated filter materials for bacteria removal. It has been shown that no single filter media could effectively remove all of the contaminants of concern in stormwater and combinations of several of filter media are necessary to achieve the removal of multiple contaminants. Field studies are also needed for stormwater filtration technologies before full scale applications. The objectives of this study were to identify filter materials that are effective at E. coli removal and evaluate the performance of media filtration for stormwater treatment under field conditions.

This project was divided into three research tasks. In Task 1, laboratory batch adsorption experiments were conducted to evaluate E. coli removal capacities of selected filter materials, which included two natural minerals (limestone and zeolite) and two industrial byproducts (recycled steel chips and steel slag). E. coli adsorption isotherms and kinetics were determined for each of the four materials. The impact of initial concentrations, temperatures, pH, NOM, and chloride concentrations on E. coli removal by the filter materials was also studied. Through the batch adsorption experiments, steel chips were identified as the most efficient material for E. coli removal. In Task 2, fixed-bed column experiments were conducted to determine E. coli removal capacities of steel chips under continuous flow conditions. Important filtration parameters, including initial concentrations, particle sizes, EBCT, and pH, were varied during the column experiments to encompass a wide range of operating conditions. Effects of NOM and intermittent flow conditions on E. coli attachment and detachment during steel chip filtration were also investigated. Real stormwater runoff samples were also used to verify the performance of steel chip filtration for E. coli removal. In Task 3, field scale experiments were conducted to investigate E. coli and phosphate removal by steel byproduct filtration under real-world stormwater runoff conditions. A mixed media filter was installed at the inlet of a stormwater detention pond in a residential area in the City of Brookings, SD. The filter media were comprised of 25% large steel slag, 12.5% small steel slag, 50% large steel chips, and 12.5% small steel chips. Four storm events between July and September 2018 were monitored to determine the treatment efficiencies of the field scale filter.

Results of the laboratory batch study showed that the E. coli removal capabilities by the four materials were in the order of steel chips > steel slag > limestone and zeolite. The quantities of E. coli attached to steel chips were 3 orders of magnitudes higher than that of steel slag, and 4 orders of magnitudes higher than that of limestone and zeolite during the adsorption isotherm experiment. E. coli adsorption onto steel chips and steel slag was favored at high temperature, low pH, low NOM, and high chloride conditions. Steel chips and steel slag showed low E. coli detachment percentages compared with limestone and zeolite during the E. coli desorption experiment.

The E. coli removal by the fixed-bed steel chip columns under standard experimental conditions (chips size = 1.0-2.0 mm, pH = 7.0, E. coli concentration = 10^6 MPN/mL, and EBCT = 10 min) varied between 89.5% and 99.2% during the 72-hour operation. Smaller steel chip sizes, longer EBCT, lower initial E. coli levels, and lower pH values resulted in higher E. coli removal efficiencies in the steel chip columns. The presence of NOM interfered with E. coli attachment to steel chips and also promoted E. coli detachment. Short-term intermittent flow temporarily decreased E. coli removal in the drained steel chip column, but the impact diminished quickly after the 30-minute operation. Short- and long-term intermittent flow did not affect E. coli removal in the undrained steel chip columns. Steel chip columns also effectively removed E. coli present in real stormwater runoff collected from parking lots and residential detention ponds.

The results of the field scale filtration study showed that the mixed media removed an average of 50% of the E. coli and an average of 42% of the phosphate in the runoff under the hydraulic retention times of 23-50 seconds. The mixed media maintained stable E. coli and phosphate removal efficiencies throughout the three-month field experiment. These results demonstrate that mixed media filtration using recycled steel chips and steel slag is an effective technology for removing E. coli and phosphate from stormwater under field conditions.

Overall, the results of this project demonstrate that recycled steel chips are highly efficient materials for E. coli removal from stormwater runoff. When mixed with steel slag, the mixed media filter exhibited excellent stormwater treatment capability for E. coli and phosphate under real-world field conditions.

6.2 Recommendations

Media filtration is a promising technology to reduce contaminant levels in stormwater runoff. Filter materials evaluation and selection are critical to the application of stormwater filtration technologies. The use of practical and cost-effective materials that possess high contaminant removal capacities would promote the full-scale filtration applications in stormwater management. In this project, recycled steel chips demonstrated high E. coli removal efficiencies through laboratory batch experiments, laboratory column experiments, and field scale filtration experiments. Recycled steel chips are readily available as an industrial byproduct at low cost. Steel chips also come with different sizes and shapes that can meet the needs of different hydraulic conditions. Therefore, we recommend that recycled steel chips can be used as a viable filter material for E. coli and phosphate removal in full-scale stormwater BMP applications.

Maintenance and longevity are two major concerns when using new filter materials for stormwater treatment. The mixed media filter with steel chips and steel slag showed stable E. coli and phosphate removal throughout the three-month field study. It is recommended that extended laboratory filtration studies and multi-year and multi-season field studies should be conducted to evaluate the longevity of steel chips for E. coli and phosphate removal. The mixing ratio of steel chips with other materials such as steel slag should also be evaluated in laboratory and field studies to determine the optimum media compositions that would maintain treatment performance and reduce filter clogging potentials.

REFERENCES

Abuladze, T., Li, M., Menetrez, M. Y., Dean, T., Senecal, A., and Sulakvelidze, A. (2008). "Bacteriophages reduce experimental contamination of hard surfaces, tomato, spinach, broccoli, and ground beef by Escherichia coli O157: H7." *Applied and Environmental Microbiology* 74(20), 6230-6238.

An, S.W., Jeong, Y.C., Cho, H.H., and Park, J.W. (2015). "Adsorption of NH4+-N and E. coli onto Mg2+-modified zeolites." *Environmental Earth Sciences* 75, 437.

APHA, AWWA, WEF, 2012. In: Rice, E.W., Baird, R.B., Eaton, A.D., Clesceri, L.S. (Eds.) (2012). "Standard Methods for the Examination of Water and Wastewater." American Public Health Association, Washington, DC.

Aziz, H.A., Othman, N., Yusuff, M.S., Basri. D.R.H., Ashaari, F.A.H., Adlan, M. N., Othman, F., Johari, M., and Perwira, M. (2001). "Removal of copper from water using limestone filtration technique determination of mechanism of removal." *Environment International* 26, 399-399.

Bai, S., and Lung, W. S. (2005). "Modeling sediment impact on the transport of fecal bacteria." *Water Research* 39 (20), 5232-5240.

Bailey, S., Olin, T.J., Bricka, R.M., Adrian, D.D. (1999). "A review of potentially low-cost sorbents for heavy metals." *Water Research* 33 (11), 2469-2479.

Carr, G. M., and Neary, J. P. (2008). *Water Quality for Ecosystem and Human Health.* UNEP/Earthprint.

Chen, J., Xiu, Z., Lowry, G.V., and Alvarez, P. (2011). "Effect of natural organic matter on toxicity and reactivity of nano-scale zero-valent iron." *Water Research* 45 (5), 1995–2001.

Chi, F. H., and Amy, G. L. (2004) "Kinetic study on the sorption of dissolved natural organic matter onto different aquifer materials: The effects of hydrophobicity and functional groups." *Journal of Colloid and Interface Science* 274 (2), 380–391.

Cho, K. H., Han, D., Park, Y., Lee, S. W., Cha, S. M., Kang, J.-H., and Kim, J. H. (2010). "Evaluation of the relationship between two different methods for enumeration fecal indicator bacteria: Colony-forming unit and most probable number." *Journal of Environmental Sciences* 22(6), 846-850.

Clark, S.E., Pitt, R. (2012). "Targeting treatment technologies to address specific stormwater pollutants and numeric discharge limits." *Water Research* 46 (20), 6715-6730.

Croxen, M. A., Law, R. J., Scholz, R., Keeney, K. M., Wlodarska, M., and Finlay, B. B. (2013). "Recent advances in understanding enteric pathogenic Escherichia coli." *Clinical Microbiology Reviews* 26(4), 822-880.

Davis, A. P., and McCuen, R. H. (2005). *Stormwater Management for Smart Growth.* Springer Science & Business Media.

DeNovio, N. M., Saiers, J. E., and Ryan, J. N. (2004). "Colloid movement in unsaturated porous media: recent advances and future directions. *Vadose Zone Journal* 3(2), 338-351.

EPA, (2009). "National Primary Drinking Water Regulations." EPA 816-F-09-004.

EPA, (2012). "Recreational Water Quality Criteria (RWQC) for Bacterial Indicators of Fecal Contamination."

EPA, (2018). "NPDES Stormwater Program." https://www.epa.gov/npdes/npdes-stormwater-program.

Foppen, J. W., Liem, Y., and Schijven, J. (2008). "Effect of humic acid on the attachment of Escherichia coli in columns of goethite-coated sand." *Water Research* 42(1–2), 211–219.

Frenzen, P. D., Drake, A., and Angulo, F. J. (2005). "Economic Cost of Illness Due to Escherichia coli O157 Infections in the United States." *Journal of Food Protection* 68(12), 2623–2630.

Hatt, B.E., Fletcher, T.D., and Deletic A. (2008). “Hydraulic and pollutant removal performance of fine media stormwater filtration systems.” *Environmental Science and Technology* 42(7), 2535-2541.

House M.A., Ellis J.B., Herricks E.E., and Hvitved-Jackson T. (1993). “Urban drainage impacts on receiving water quality.” *Water Science and technology* 27(12), 117-158.

Hozalski, R. M., Bouwer, E. J., and Goel, S. (1999). “Removal of natural organic matter (NOM) from drinking water supplies by ozone-biofiltration.” *Water Science and Technology* 40(9), 157-163.

Ishii, S., Ksoll, W.B., Hicks, R.E., and Sadowsky, M.J. (2006). “Presence and growth of naturalized E. coli in temperature soils from Lake Superior watershed.” *Environmental Microbiology* 72(1), 612-621.

Jeng, H., Englande, A.J., Bakeer, R.M., and Bradford, H.B. (2005). “Impact of urban stormwater runoff on estuarine environmental quality.” *Estuarine, Coastal and Shelf Science* 63(4), 513-526.

Johnson, W.P., and Logan, B.E. (1996). “Enhanced transport of bacteria in porous media by sediment-phase and aqueous-phase natural organic matter.” *Water Research* 30(4), 923- 931.

Kim, L.H., Kang, H.M., and Bae, W. (2010). “Treatment of particulates and metals from highway stormwater runoff using zeolite filtration.” *Desalination and Water Treatment* 19 (1-3), 97-104.

Kim, L.H., Kang, H.M., and Bae, W. (2012). “Treatment of particulates and metals from highway stormwater runoff using zeolite filtration.” *Desalination and Water Treatment* 19(1-3), 97-104.

Kunkel, E.A., Privette, C.V., Sawyer, C.B., and Hayes, J.C. (2013). “Attachment of Escherichia coli to fine sediment particles within construction sediment basins.” *Advances in Bioscience and Biotechnology* 04 (03), 407-414.

Liu, Z., Lompe, K.M., Mohseni, M., Berube, P.R., Sauve, S., and Barbeau, B. (2020). “Biological ion exchange as an alternative to biological activated carbon for drinking water treatment.” *Water Research*, 168, 115148.

Lukasik, J., Cheng, Y., Lu, F., and Tamplin, M. (1999). “Removal of microorganisms from water by columns containing sand coated with ferric and aluminum hydroxides.” *Water Research* 33, 769-777.

Mallin, M. A., Johnson, V. L., and Ensign, S. H. (2009). “Comparative impacts of stormwater runoff on water quality of an urban, a suburban, and a rural stream.” *Environmental Monitoring and Assessment* 159(1-4), 475-491.

Mohanty, S. K., Torkelson, A. A., Dodd, H., Nelson, K. L., and Alexandria B. (2013). “Engineering solutions to improve the removal of fecal indicator bacteria by bioinfiltration systems during intermittent flow of stormwater.” *Environmental Science and Technology*, 47(19), 10791–10798.

Mohanty, S. K., and Boehm, A. B. (2014). “Escherichia coli removal in biochar-augmented biofilter: Effect of infiltration rate, initial bacterial concentration, biochar particle size, and presence of compost.” *Environmental Science and Technology* 48(19), 11535–11542.

Morgan, B., and Lahav, O. (2007). “The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O_2 in aqueous solution - basic principles and a simple heuristic description.” *Chemosphere* 68(11), 2080–2084.

Muirhead, R. W., Collins, R. P., and Bremer, P. J. (2006). “Interaction of Escherichia coli and soil particles in runoff.” *Applied and Environmental Microbiology*, 72(5), 3406–3411.

Noble, R. T., Weisberg, S. B., Leecaster, M. K., McGee, C. D., Ritter, K., Walker, K. O., and Vainik, P. M. (2003). “Comparison of beach bacterial water quality indicator measurement methods.” *Environmental Monitoring and Assessment* 81(1-3), 301-312.

Paul, M. J., and Meyer, J. L. (2001). “Streams in the Urban Landscape.” *Annual Review of Ecology and Systematics*, 32, 333–365.

Penn, C. J., Mcgrath, J. M., Rounds, E., Fox, G., and Heeren, D. (2012). "Trapping phosphorus in runoff with a phosphorus removal structure." *Journal of Environment Quality*, 41(3), 672-679.

Prabhukumar, G. (2013). "Development of permeable reactive filter systems (PRFS) for treatment of urban stormwater runoff." Dissertation of Illinois Institute of Technology.

Reddy, K.R., Xie, T., and Dastgheibi, S. (2014a). "Removal of heavy metals from urban stormwater runoff using different filter materials." *Journal of Environmental Chemical Engineering* 2, 282-292.

Reddy, K.R., Xie, T., and Dastgheibi, S. (2014b). "Mixed-media filter system for removal of multiple contaminants from urban storm water: large-scale laboratory testing." *Journal of Hazardous, Toxic, and Radioactive Waste* 18(3), 04014011.

Rijnaarts, H. H. M., Norde, W., Lyklema, J., and Zehnderet A.J.B. (1995). "The isoelectric point of bacteria as an indicator for the presence of cell surface polymers that inhibit adhesion." *Colloids and Surfaces B: Biointerfaces* 4(4), 191–197.

SD DENR., (2018). "The 2018 South Dakota Integrated Report for Surface Water Quality Assessment." South Dakota Department of Environment and Natural Resources, Pierre, SD, 2018.

Selegean, J., Kusserow, R., Patel, R., Heidtke, T., and Ram, J. (2001). "Using zebra mussels to monitor Escherichia coli in environmental waters." *Journal of Environmental Quality* 30(1), 171-179.

Seelsaen, N., McLaughlan, R., Moore, S., Ball, J.E., and Stuetz, R.M. (2006). "Pollutant removal efficiency of alternative filtration media in stormwater treatment." *Water Science Technology* 54 (6-7), 299-305.

Smith, V., Tilman, G., and Nekola, J. (1999). "Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems." *Environmental Pollution*, 100(1-3), 179–196.

Starosvetsky, J., Cohen, T., Cheruti, U., Bilanovic, D., and Armon, R. (2012). "Effects of physical parameters on bacterial cell adsorption onto pre-imprinted sol-gel films." *Journal of Biomaterials and Nanobiotechnology* 3, 499-507.

Stumm, W., and Lee, G. F. (2007). "Oxygenation of ferrous iron." *Industrial & Engineering Chemistry*, 53(2), 143–146.

Tafuri A.N., and Field R. (2012). "Treatability aspects of urban stormwater stressors." *Frontiers of Environmental Science and Engineering* 6(5), 631-637.

UN, (2014). "World Urbanization Prospects: The 2014 Revision-Highlights." United Nations.

Van Der Wal, A., Minor, M., Norde, W., Zehnder, A.J.B., and Lyklemaet J. (1997). "Electrokinetic potential of bacterial cells." *Langmuir* 13(2), 165–171.

Wackernagel, M., and Rees, W. (1998). *Our Ecological Footprint: Reducing Human Impact on the Earth*. New Society Publishers.

Wium-Anderson, W., Nielsen, A.H., Hvitved-Jacobsen, T., Kristensen, N.K., Brix, H., Arias, C., and Vollertsen, J. (2012). "Sorption media for stormwater treatment-A laboratory evaluation of five low-cost media for their ability to remove metals and phosphorus from artificial stormwater." *Water Environment Research*, 84 (7), 605-616.

Wu, T., Liu, Z., Zhu D., and Chen, Y. (2019). "Effect of the particle size and surface area on Escherichia coli attachment to mineral particles in fresh water." *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 54(12), 1219–1226.

Yousef, R. I., El-Eswed, B., and Al-Muhtaseb, A. H. (2011). "Adsorption characteristics of natural zeolite as solid adsorbents for phenol removal from aqueous solution: kinetics, mechanism and thermodynamics studies." *Chemical Engineering Journal* 171, 1143–1149.