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Laboratory Evaluation of Internal and External Nutrient Removal to Control Algal Bloom in Eutrophic Lakes

Sepideh Sadeghi
South Dakota State University

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LABORATORY EVALUATION OF INTERNAL AND EXTERNAL NUTRIENT REMOVAL TO CONTROL ALGAL BLOOM IN EUTROPHIC LAKES

BY

SEPIDEH SADEGHI

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This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy in Civil Engineering degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Guanghui Hua, PhD
Dissertation Advisor Date

Nadim Wehbe, PhD
Head, Civil and Environmental Engineering Date

Dean, Graduate school Date

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CONTENT

LIST OF ABBREVIATIONS

Al	Aluminum
$AlOH_3$	Aluminum hydroxide
BB	Bidentate binuclear
BM	Bidentate mononuclear
BOD	Biological Oxygen Demand
Ca	Calcium
$Ca_3(PO_4)_2$	Calcium phosphate
COD	Chemical Oxygen Demand
CO_2	Carbon dioxide
$CaCO_3$	Calcium carbonate
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DBPs	Disinfection byproducts
HA	Humic acid
H_2S	Hydrogen sulfide gas
HRT	Hydraulic retention time
La	Lanthanum
$La(OH)_3$	Lanthanum hydroxides
NaOH	Sodium hydroxide
NTU	Nephelometric Turbidity Unit
NOM	Natural Organic Matter

NO_3-N	Nitrate as nitrogen
NO_2- N	Nitrite as nitrogen
N_2O	Nitrous oxide
NO	Nitric oxide
N_2	Nitrogen gas
NH_4^+	Ammonium
PAC	Poly Aluminum Chloride
PO_4-P	Phosphate as P
SiO_2	Silicon dioxide
SO_4^{2-}	Sulfate
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus

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ABSTRACT

LABORATORY EVALUATION OF INTERNAL AND EXTERNAL NUTRIENT REMOVAL TO CONTROL ALGAL BLOOM IN EUTROPHIC LAKES

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Eutrophication is one of the most widespread water quality problems in lakes and reservoirs. Frequent cyanobacterial blooms resulting from eutrophication can greatly damage aquatic ecosystems and pose a high risk to human health. Phosphorus (P) and nitrogen (N) are the major causes for eutrophic conditions and can enter to the aquatic ecosystem via different sources. The combination of phosphorus precipitation and sediment capping are promising technologies to minimize internal P loading and control harmful algal blooms in eutrophic lakes. Denitrification bioreactors have emerged as an important edge-of-field treatment technology to reduce nitrate-nitrogen loads from external sources. The objective of this study was 1) to evaluate the use of natural minerals to enhance the precipitation of phosphorus and cyanobacteria during alum coagulation, 2) to reduce phosphate release during sediment capping, 3) to evaluate the synergistic effects of polyaluminum chloride (PAC) and phoslock on phosphate and cyanobacteria removal during coagulation of eutrophic lake water, and 4) to evaluate the quantity and quality of dissolved organic carbon (DOC) leaching from agricultural residues including corn cobs, corn stover and barley straw to develop a new denitrification bioreactor system that uses a combination of an agricultural residue and woodchips for enhancing the nitrate removal efficiency.

Laboratory coagulation experiments were conducted on a lake water spiked with Anabaena sp. using alum and four natural minerals (zeolite, calcite, limestone, and sand) to determine the effect of natural minerals on chlorophyll α, phosphate and turbidity removal. Long-term column sediment capping experiments were also conducted using different minerals after alum coagulation to evaluate their effectiveness in reducing phosphate release. The results showed that alum coagulation was able to remove 85-90% of phosphate and chlorophyll α from Anabaena sp. enriched lake water samples. The added natural particles did not substantially affect the removal of phosphate and chlorophyll α during combined alum and particle coagulation. However, natural particles substantially increased the floc settling kinetics during coagulation. The combined treatment with alum and particles also increased the resistance of the sediment to disturbance by mixing. The long-term sediment capping experiments showed that capping with natural minerals substantially reduced the levels of phosphate released from the sediment.

Lake water samples were also treated with PAC, phoslock, and the combination of these two technologies to evaluate their removal efficiencies for phosphate, chlorophyll α, and DOC. The impact of doses, pH, DOC levels on the removal efficiencies were investigated. The results showed that PAC alone achieved 90% removal for phosphate and chlorophyll α, and 23.6% removal for DOC at the maximum dose of 8 mg Al/L. Phoslock alone removed phosphate, chlorophyll α, and DOC by 70%, 73.3% and 4%, respectively, at a dose of 800 mg/L. The combination of PAC (4 mg Al/L) and phoslock (300 mg/L) resulted in the removal of phosphate, chlorophyll α, and DOC by 90%, 100%, and 35%, respectively, suggesting that the combination of PAC (4 mgAl/L) and phoslock (300 mg/L) is able to significantly enhance the phosphate, chlorophyll α, and DOC removal

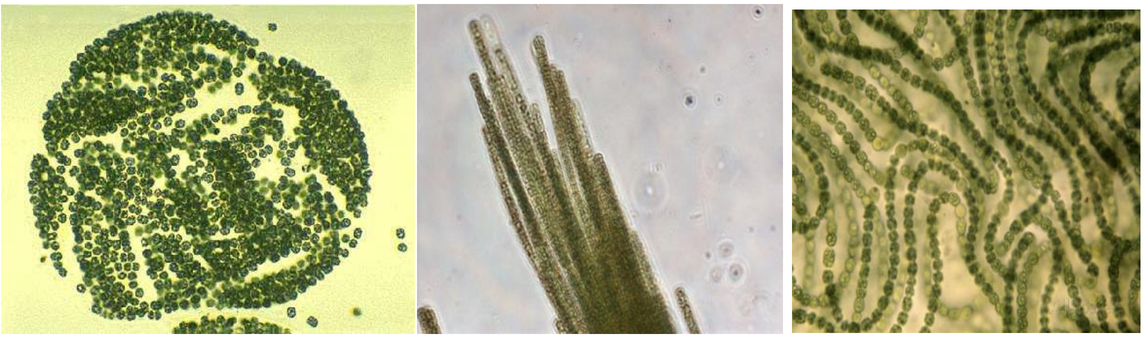
efficiencies. The combined use of PAC and phoslock exhibited high tolerances to variations in pH and DOC levels for phosphate and chlorophyll α removal. The combination of PAC and Phoslock also increased the settling kinetics of the flocs.

The final set of experiments showed that the DOC leaching potential followed the order of barley straw > corn stover > corn cobs > woodchips. Agricultural residues also exhibited faster DOC leaching kinetics and higher biodegradation potentials than woodchips. Although agricultural residues leached higher concentrations of nutrients during initial flush, those concentrations quickly declined within several days of leaching.

CHAPTER 1: INTRODUCTION

1.1 Algal blooms

Excessive amount of nutrient loading to the surface water is one of the major reasons for cyanobacteria (blue-green algae) blooms. Cyanobacteria are the microscopic bacteria found in surface waters and wet soils. Cyanobacteria photosynthesize like algae and they are able to move through the layers of water to obtain light and nutrients. They move to the surface of water to get light to photosynthesize and go to the bottom of water to get nutrients at night. Depending upon the species, cyanobacteria can occur as single cells, filaments of cells, or colonies. When they grow in colonies, they appear as a blue-green color on the top of water. Cyanobacteria contain a characteristic pigment which gives the group their blue-green coloration. When cyanobacteria blooms begin to die and disintegrate, this pigment may color the water a distinctive bluish color. Algal blooms can cause undesirable water pollution including high turbidity, dissolved oxygen deficiency, taste and odor (Blaha et al., 2009). Three genera of cyanobacteria account for the vast majority of blooms, including toxic blooms, world-wide: Anabaena, Aphanizomenon (they typically develop in late spring or early summer), and Microcystis (typically bloom in mid-summer or in autumn). Different cyanobacteria species are shown in Figure 1. Cyanobacteria can produce several toxins, but two types of toxins are of particular concern which are: microcystins and anatoxin-A. Microcystins are a group of hepatoxins (toxins that affect the liver). Microcystins are very stable and do not break down quickly in water. Microcystins are considered to be the most commonly-found cyanobacterial toxins in water and are the toxins most responsible for human and animal poisonings after swimming or drinking the cyanobacteria-contaminated water (Blaha et al., 2009). Anatoxin-A is a potent neurotoxin (toxins that affect the nervous system) that can cause lethargy, muscle aches, confusion, memory impairment, and, at sufficiently high



(a) (b) (c)

Figure 1. Different cyanobacteria species; Microcystis (a), Aphanizomenon (b), Anabaena (c)

concentrations, death (Department of Ecology of Washington, 2017). Characteristics of different species of cyanobacteria are shown in Table 1.

Cyanobacteria blooms affect both ecosystem health and economy. The majority of cyanobacteria bloom toxin research has focused on mammalian toxicity. However, toxic blooms have been frequently involved in many incidents of fatal animal poisonings. Moreover, a wide range of aquatic organisms is directly exposed to the toxic contained in their food (phytoplanktivorous fish, zooplankton etc.) and/or to toxins dissolved in water, which may cause diverse effects (Blaha et al., 2009). Recreational activities may be impacted by heavy algal blooms (Dodds et al., 2009). Moreover, water users are less likely to swim, boat and fish during algal blooms due to health risks, unfavorable appearance, or unpleasant odors (Zampares and Zacharia, 2014). Drinking water supplies can also be affected by algal blooms. The treatment of algae impacted water is costly due to the presence of toxins.

1.2 Eutrophication

Excessive amounts of nutrients (phosphorous (P) and nitrogen (N)) coming to the water from external sources is one major cause of algal blooms. Phosphorous and N are found in fertilizer, livestock waste, sewage discharges, industrial effluents, soil erosion, and detergents. Extensive use of fertilizers results in significant concentrations of nutrients in agricultural runoff which enters to the surface water is known as the major cause of eutrophication (Figure 2).

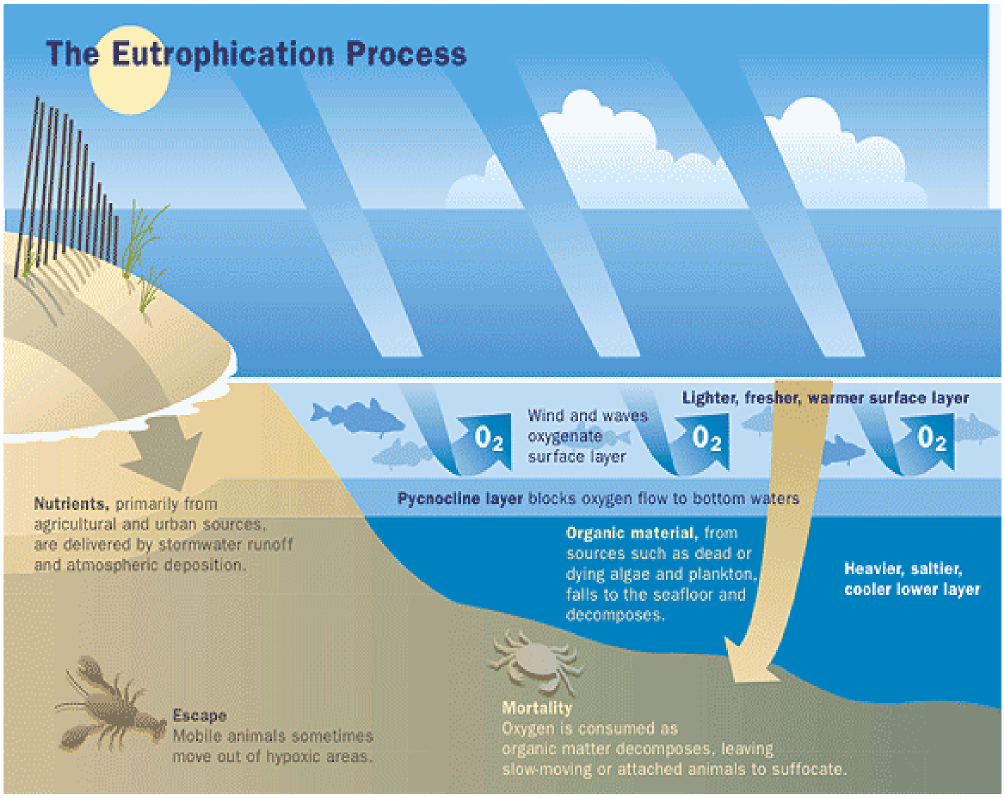


Figure 2. How eutrophication affects a water system (Treehugger, 2017)

Phosphorus is generally the limiting nutrient in surface water systems. Phosphorus concentration in unpolluted waters vary from less than 1 part per billion (ppb) to more than 200 ppb, depending on local geology and the natural level of organic material in the water (Wetzel, 1983). Lakes and reservoirs can be classified according to the extent of their eutrophication (or nutrients enrichment) into four main classes: oligotrophic, mesotrophic, eutrophic and hypereutrophic (Table 2).

Table 2. A classification of lakes according to the extent of their eutrophication (UNEP, 2017)

Parameters	Oligotrophic	Mesotrophic	Eutrophic	Hypereutrophic
Average Total P	8 µg/L	26.7 µg/L	84.4 µg/L	>200 µg/L
Average Total N	661 µg/L	753 µg/L	1875 µg/L	High

This classification results from extensive examination of eutrophication by the Organization for Economic Cooperation and Development (OECD) in the 1970s and early 1980s (UNEP, 2017). The internal nutrient loading from nutrient-rich sediment is another major factor that is responsible for enhanced eutrophication processes (Figure 3), and many studies have shown that the lake recovery is a slow process even when the external nutrient loading has been substantially reduced (Gulati and Van Donk, 2002; Berg et al., 2004; Cooke et al., 2005).Nutrients released from the sediment can delay the lake recovery for years to decades (Sondergaard et al., 2001; Cooke et al., 2005).

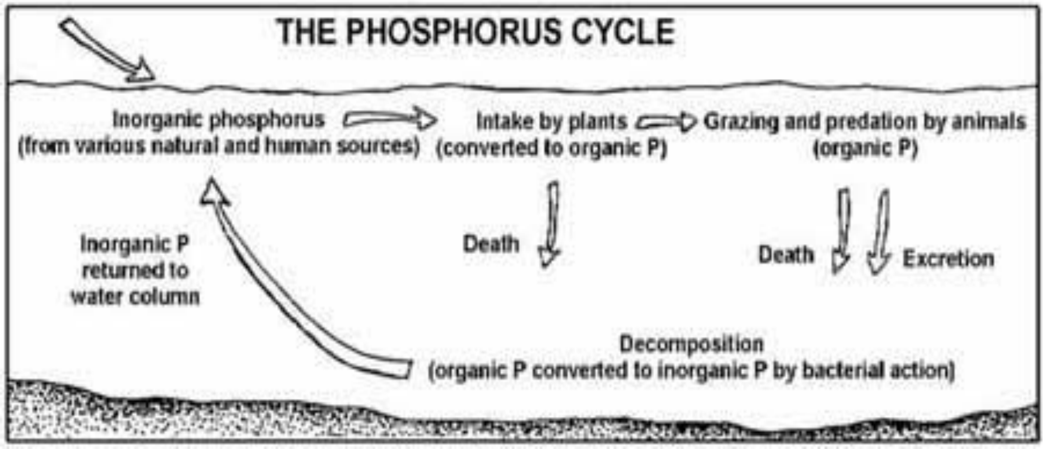


Figure 3. Internal source of P (EPA, 2017)

1.3 Eutrophication control; in-lake and in-sediment phosphorous control

Phosphorous is the most important nutrient responsible for the eutrophication of surface water due to its excess bioavailability. There is no source of atmospheric P that is bio-available like nitrogen. Therefore, the control of P is more feasible than nitrogen (Zamparas and Zacharias, 2014). Direct precipitation of P is an effective remedial method that can quickly reduce the lake water P content. Aluminium-, calcium-, and iron salts are the common chemical coagulants that have been applied for P reduction in lakes (Cooke et al., 2005). In-situ sediment capping technology has been also developed to control P cycling from the sediment.

1.3.1 Alum treatment

Aluminum salts are common in water treatment and have been used in lake water restoration too. Alum performs optimally at pH values ranging from 6-8, and is effective in precipitating suspended particulates and absorbing and removing soluble forms of P such as dissolved phosphorous fractions. Churchill et al. (2008) reported phosphate concentration reductions by 84% using 5 mg Al/L as alum to decrease phosphate from 0.13 mg P/L to below 0.02 mg P/L in Matthiesen Creek Lake. Pilgrim et al. (2007) also reported greater than 90% total phosphate removal from lake water using alum doses of 4-8 mg Al/L. Similar studies were reported by Mason et al. (2005) and Trejo-Gaytan et al. (2006) for total phosphate removal from surface water. They reported greater than 90% total phosphate removal using an alum dose of around 4 mg Al/L. Paul et al. (2008) showed the impact of alum on the water nutrient concentrations in Lake Okaro, New Zealand. The study by Lewandowski et al. (2003) showed the long term effects of P precipitations with alum in hypereutrophic Susser See Lake in Germany. The alum application into an oligomictic lake to observe the effectiveness of the microfloc injection system was reported by Moore et al, (2009) for Newman Lake located in Washington, USA. The short term effects of buffered alum treatments on lake sediment P speciation was also reported by Dugopolski et al, (2008) in Green Lake located in Washington USA. The results showed that although chemical and physical precipitation can remove the total P from the water column, the treatment results in low density flocs, causing turbidity over an extended period of time. Treatment does not also provide a long-term prevention of P release from the sediment due to the resuspension of the precipitated flocs. Moore and Christensen (2009) used alum for the treatment of Newman Lake in Washington State in 1997. Although total P concentration decreased significantly in that treatment attempt, in the next two years P concentration increased to the pre-restoration levels which showed the ineffectiveness of the treatment (Moore and Christensen, 2009).

1.3.2 Sediment removal

Internal P loading originates from a pool accumulated in the sediment. Phosphorous release from the sediment to the overlaying water can delay improvement of water quality for years to decades (Sondergaard et al., 2005). Therefore, effective internal P loading control methods are necessary to accelerate lake recovery and achieve long-term mitigation of lake eutrophication. Sediment removal is recommended as one way to inhibit P recycling from the sediments (Moss et al., 1996). This method has limitations in operating cost and implementation and typically cannot provide a permanent solution. Phillips et al. (1999) reported that although new sediment which replaced the contaminated sediment in Alderfen Broad (UK) had lower P concentration, within a year the total P concentration in the new sediment had increased to 80% of its original value.

1.3.3 Sediment Capping

In-situ sediment capping technology has been developed to control P cycling from the sediment. This technology involves placement of a layer of particulate materials at the sediment-water interface to create a barrier between the sediment and overlaying water. In-situ sediment capping is a promising technology that can stabilize sediment, minimize re-suspension, and reduce nutrient release from the sediment (Simpson et al., 2002; Kim et al., 2007; Lin et al., 2011). Clean sand has traditionally been used for in situ capping of sediment for eutrophication control. Pan et al. (2012) used sand capping to decrease the P release from the sediment in 20 days of sediment incubation. They reported the P concentration in the water column was 2.13 mg P/L in the control after 20 days. This was reduced to 0.4 mg P/L in the sand capping treated system after an incubation period. Yin and Kong (2015) used 700˚C-heated natural calcium-rich attapulgite (NCAP700) as a low-cost P-capping agent to reduce internal P-loading in lake sediments. Their study showed that NCAP700 could effectively reduce P release from the sediment during a 40-day remediation. Recently, an active barrier system (ABS) has been developed to improve the effectiveness of sediment capping. In this system, reactive materials are used to bind containments in the sediments by adsorption or precipitation, thereby improving capping efficiency. These reactive materials include activated carbon, gypsum, modified sand, natural and modified zeolite, calcite, modified soil and clays and others (Berg et al., 2004; Jacobs and Waite, 2004; Park et al., 2007; Viana et al., 2008; Pan et al., 2012). It was reported that the P was reduced by more than 99% from 2.13 mg P/L to less than 0.01 mg P/L by using chitosan modified soil as a capping material compared with the control system on day 20 of sediment incubation (Pan et al., 2012). Several studies have shown that calcite is effective in preventing phosphorus release from sediment under anaerobic conditions (Hart et al., 2003; Berg et al., 2004; Lin et al., 2011). Lin et al. (2011) reported that the efficiency of the ABS using calcite for reducing P release from the sediments considerably depended on the barrier thickness, and it significantly increased with the increase of the barrier thickness. They also found the incorporation of natural zeolite into the ABS using calcite greatly increased the efficiency of the ABS to reduce P release from anaerobic sediments (Lin et al., 2011). Gibbs and Ozkundakci (2010) showed that modified zeolite was an effective sediment capping material which completely blocked the release of P from the sediments under anoxic conditions. It was also reported by Yang et al. (2014) that the addition of Zirconium-modified zeolite into the lake sediment could reduce the potential of phosphate release from the sediment as well as increase the P adsorption capacity of the sediment. A lanthanum-enriched benthonite clay (Phoslock) has been also shown to be a strong P binding material in several laboratory and field experiments (Lurling and Van Oosterhout, 2013; Noyma et al., 2015). These P binding materials can be used as active barrier systems for sediment capping in eutrophic lakes to provide long-term inhibition of P recycling from the sediments. Meis et al. (2012) investigated the short term alternations in sediment lanthanum composition and sediment P-fractions before and after the application of phoslock in Clatto Reservoir Dundee, UK. Robb et al. (2003) also used phoslock to remove P from the water column and sediment in Swan Canning and Vasse Wonnerup estuaries, Australia. Van Oosterhout and Lurling (2011) worked on a novel restoration technique “flock and lock” using phoslock for Lake Rauwbraken, the Netherlands.

1.4 Cyanobacteria blooms control

There are various methods to control cyanobacteria blooms. One example is reducing the amount of nutrients that get into the water. There are also some ways of treating the blooms including physical removal, chemical procedures and biological inactivation. The most commonly used method is using chemical salts or clays. Poly aluminum chloride (PAC) as a coagulant salt with and without phoslock was used to remove cyanobacteria from the water sample of Lake Rauwbraken located in the Netherlands (Lurling and Oosterhout, 2013). According to the results, the relatively low dose of the PAC (2.2 and 4.4 mg Al/L) was insufficient to sediment cyanobacteria, and the phoslock alone in 390 mg/L was insufficient to sediment the cyanobacteria. But the combination of PAC and phoslock effectively settled cyanobacteria flocs. Fast et al. (2014) compared the ultrasound-alum and ultrasound-chitosan flocculation of algal turbid water.

The results showed that although the alum removal efficiency is higher than chitosan, the use of chitosan as a coagulant may offer benefits such as environmental-friendliness and small volumes of non-toxic sludge. Noyma et al. (2015) evaluated the efficacy of PAC and chitosan, alone and combined with different doses of phoslock and local red soil to sediment cyanobacteria from Funil Reservoir, Brazil. The results indicated that cyanobacteria could be flocked and effectively precipitated using a combination of PAC or chitosan with phoslock and local red soil. Pan et al. (2006) used three different types of clays for cyanobacteria flocculation. They found that sepiolite, talc, ferric oxide, ferro ferric oxide and kaolinite had much higher abilities to flocculate cyanobacteria cells than other clays. They also found that the dosage of clay had a key role in the removal process. As the clay loading decreased the flocculating ability of clays significantly decreased. Jiang and Kim (2008) compared algal cell removal by clays and Al-based coagulants. They found that PAC achieved a better performance in removing algal cells in comparison with aluminum sulphate. Bentonite and montmorillonite clays both achieved 100% algal cell removal which is greater than that the PAC achieved. The study proposed that the microstructure of clay-algae flocs play important roles to contribute to a good performance of algae removal. Huang et al. (2016) used PAC-modified clay (PAC and diatomite) as an efficient flocculating agent in algal bloom control. The results showed that a dosage of 1.8 g/L PAC-modified clay (0.8 g/L PAC and 1 g/L diatomite) could reduce turbidity by more than 90% in 1 h.

1.5 External source of nitrate and emerging denitrification bioreactors

Agricultural subsurface drainage is a widely adopted water management practice to increase crop production in the Midwestern United States. Although subsurface drainage removes excess water from the soil which allows cultivation of agricultural fields with poor natural drainage, this practice can lead to the transport of nitrate from agricultural fields to surrounding natural water. High nitrate levels in surface waters can result in several water quality impacts such as harmful algal blooms, hypoxic zones, and contamination of drinking water supplies. Therefore, it is necessary to develop technologies to remove nitrate in subsurface drainage to protect natural water resources. Nitrate-nitrogen loadings in Midwestern drainage often do not meet the EPA standard of 10 mg NO_3^--N/L (USEPA, 2011). Typical nitrate loading from agricultural soils in Midwest area is 25-35 kg N/ha (Jaynes et al., 1999; Kalita et al., 2006; Lawlor et al., 2011). The nitrate loading can reach as high as 81 kg N/ha (Kaspar et al., 2007) and 88 kg N/ha (Lawlor et al., 2008). Denitrification bioreactors have emerged as an important edge-of-field treatment technology to reduce nitrate loads from external nutrient sources like agricultural drainage. These bioreactors typically utilize an organic carbon medium to support the growth of denitrifying bacteria to convert nitrate to nitrogen gas (Greenan et al., 2006).

Denitrification occurs when NO_3^- reduces to N_2 by the following equation (Christianson, 2011):

$$5\ C + 4\ NO_3^- + 2\ H_2O \rightarrow 2\ N_2 + 4\ HCO_3^- + CO_2 \qquad \text{Eq. 1.1}$$

The requirements for denitrification to proceed are included; (1) denitrifying bacteria, (2) electron acceptor (e.g. NO_3^-, NO_2^-, NO, N_2O), (3) carbon source as electron donor (e.g. woodchips), and (4) limited dissolved oxygen (DO) (Korom, 1992). Under saturated conditions, bacteria utilize oxygen to oxidize the available carbon. When oxygen concentrations become limiting, facultative anaerobes become active using NO_3^- as electron acceptors in their respiration electron transport chain (Korom, 1992). Dissolved oxygen concentrations of 0.2 mg/L can inhibit denitrification from reaching maximum rates (Metcalf and Eddy, 2003). Denitrifying bacteria are mostly facultative anaerobes, both autotrophic and heterotrophic denitrifiers, but most are heterotrophic (Korom, 1992). Organic materials is the common source of electrons for reactions and it yields the most energy for these heterotrophs (Korom, 1992). Woodchips are the most commonly used materials in denitrification bioreactors for subsurface drainage treatment and have shown the ability to provide long-term (> 10 years) nitrate removal while requiring minimum maintenance (Blowes et al., 1994; Robertson, 2010; Cooke and Bell, 2014).

1.5.1 Denitrification bioreactors Concerns

The most concerns about the application of denitrification process for subsurface drainage treatment include greenhouse gas production like N_2O, organic matter leaching from the carbon source, and sulfate reduction (Schipper et al., 2010).

Organic flushing

Many studies showed that several organic and inorganic contaminants including TOC/DOC, BOD, NH_4^+, and TKN could leach to the reactor effluent during the start-up of a denitrification bioreactor (Cameron and Schipper, 2010; Gibert et al., 2008; McLaughlan and Al-Mashaqbeh, 2009; Schipper and Vojvodic-Vukovic, 1998). The initial dark colored effluent which is often observed in the beginning of the bioreactor process could contain very high organic content (Schipper et al., 2010), though the leach of organic carbon appears to stabilize at lower rates over time (Robertson et al., 2005). High concentrations of DOC in surface waters may cause oxygen depletion and lead to the formation of disinfection byproducts (DBPs) during the drinking water disinfection processes (Singer, 1999; Xie, 2003; Pan et al., 2016). To mitigate this organic leaching many researchers suggested the use of pre-flushed materials (Diaz et al., 2003). Although this is practical in lab-scale experiments, it is logistically difficult at field-scale applications. McLaughlan and Al-Mashaqbeh, (2009a) evaluated the significance of particle size on the mass and rate of DOC release from composted garden organics, pine and hard wood. They reported in general, the largest particle size has the lowest cumulative leached DOC for all the materials, and that compost leached higher amounts of DOC than pine and hardwood (McLaughlan and Al-Mashaqbeh, 2009a).

Nitrous oxide

N_2O can be released in denitrification bioreactors due to incomplete denitrification (Warnekea et al., 2011a). Higher DO inlet concentrations led to incomplete denitrification which increased production of dissolved N_2O (Elgood et al., 2010). Special environmental conditions like low pH, temperature, C:N ratio, or fluctuating flow rates are other reasons responsible for incomplete denitrification (Chapin III et al., 2002). Christianson (2011) tested the effect of fluctuating flow rates on N_2O emissions. They found small spikes of N_2O were released when water levels dropped in the reactors, but overall the N_2O released was never more than 1% of the influent NO_3^- (Christianson, 2011).

Sulfate reduction

Sulfate (SO_4^{2-}) reduction usually occurs when NO_3^- has been completely removed in the denitrification process. Sulfate reduction typically takes place at high hydraulic detention times and high temperatures (Blowes et al., 1994; Robertson and Cherry, 1995; Van Driel et al., 2006; Robertson and Merkley, 2009). The use of SO_4^{2-} as an electron acceptor is not as favorable as NO_3^-, but when NO_3^- is reduced completely in a bioreactor, SO_4^{2-} reducing organisms can out-compete denitrifiers for carbon and convert naturally present SO_4^{2-} to hydrogen sulfide gas (H_2S) (Christianson, 2011). The major concerns about sulfate reduction include loss of carbon for the denitrifiers and the production of H_2S.

1.6 Denitrification bioreactor performance factors

Many studies investigated the different denitrification bioreactor performance factors like temperature, hydraulic retention time (HRT), carbon substrate, flow rates, carbon source size and mass, pH, initial dissolved oxygen, and initial nitrate concentrations on nitrate removal as well as dissolved organic carbon (DOC) leaching and green gas production.

Different carbon substrate and temperature

Cameron and Schipper (2010) used different carbon substrates in denitrification bioreactors to compare their nitrate removal, hydraulic and nutrient leaching characteristics over a 23 month period. They did the experiments at two different temperatures 14 and 23.5 ^oC. The results showed that mean nitrate removal rates were 19.8 and 15g N/ m^3-d (maize cobs), 7.8 and 10.5g N/ m^3-d (green waste), 5.8 and 7.8 g N/ m^3-d (barley straw), 3.0 and 4.9 g N/ m^3-d (softwood), and 3.3 and 4.4 g N/ m^3-d (hardwood) for the 14 and 23.5 ^oC treatments, respectively. Maize cobs provided a 3–6.5 fold increase in nitrate removal compared to wood media, without prohibitive decreases in hydraulic conductivity, but had higher rates of nutrient leaching at start-up. Significant differences in removal rate occurred between the 14 and 23.5 ^oC treatments. Long-term nitrate removal rates were 1.5 times higher at the 23.5 ^oC barrels than at the 14 ^oC barrels. However, long-term nitrate removal rates for maize cob media were lower in the 23.5 ^{o}C barrels than in the 14 ^{o}C barrels.

Hydraulic flow rate

Greenan et al. (2009) investigated the effect of different flow rates of 2.9, 6.6, 8.7 and 13.6 cm^3/d on the ability of wood chip bioreactors to remove nitrate. The initial concentration of nitrate was 50 mg /L. The remaining nitrate concentrations in the effluent were 0.0, 18.5, 24.2, and 35.3 mg/ L for the flow rates 2.9, 6.6, 8.7, and13.6 cm^3/d, respectively, which correspond to 100, 64, 52, and 30% removal efficiency. According to these results, denitrification performance of woodchip bioreactors increased with increasing detention times. Increasing flow rate could also enhance the chance of oxygen transferred to the denitrification process which may lead to nitrate removal reduction. In addition, N_2O production from the columns was determined in this study, and it accounted for 0.003-0.028% of the N denitrified, indicating near complete denitrification.

Retention time, limestone addition, and woodchip species, size, and mass percentage

Peterson et al (2015) investigated the effects of storm water retention time, limestone addition, and woodchip species, size, and mass percentage on the bioretention denitrification process. Based on the results, a 0.8-day average retention time showed the highest nitrate removal percentage of 82.4 ± 0.4%. Willow Oak and Red Maple woodchips were more effective at total nitrogen removal than Wild Cherry, Virginia Pine, and American Beech wood chips. Smaller woodchips and higher woodchip mass percentage corresponded to greater nitrate removal efficiencies, but also higher organic nitrogen leaching. Media containing 4.5% 5-mm Willow Oak woodchips by mass represented optimum conditions. In addition, they investigated the effect of limestone on nitrate removal. They found that adding limestone at 5 and 10%, while raising the pH, did not increase the NO_3^--N removal efficiency of the system.

Wood age and hydraulic retention time

Hoover et al (2016) evaluated initial woodchip age on the release of total organic C during reactor start up for fresh and weathered woodchips, and a range of hydraulic retention times (2-24 h), initial nitrate concentrations (10, 30 and 50 mg N/L) and temperatures (10, 15, and 20 °C) on nitrate removal. The results revealed that greater TOC was released during bioreactor operation with fresh woodchips, whereas organic C release was low when the columns were packed with naturally weathered woodchips. Nitrate-N concentration reductions increased from 8 to 55% as HRT increased from 2 to 24 h. Nitrate–N removal decreased at an influent concentration of 10 mg/ L, but increased at influent concentrations of 30 and 50 mg/ L. NO_3^--N removal also increased as temperature increased. Healy et al. (2015) considered different HRTs ranging from 4 to 22 d for denitrifying reactors. They used lodgepole pine woodchips (LPW), lodgepole pine needles (LPN), barley straw (BBS) or cardboard as different carbon sources. They found that all bioreactors performed best at HRTs of around 5 days. The LPN media showed the highest ability to remove nitrate across all HRTs. However, this carbon source lost around 80% of the initial organic content in a relatively short period. This indicates that a more commonly available bioreactor media, such as LPW, may be more suitable for the long-term operation of bioreactors. Moreover, the cardboard bioreactor contained the highest abundance of denitrifying microorganisms compared with the other bioreactors, indicating that the source of carbon influenced the quantity of denitrifying microbes. Moorman et al. (2010)

observed denitrification bioreactor performance over 9 years in the field. They found that loss of wood (as the carbon source) through decomposition after 9 years reached 75% at the 90–100 cm depth with a wood half-life of 4.6 years. However, wood loss was less than 20% at 155–170 cm depth and the half-life of this wood was 36.6 years. Denitrification potentials ranged from 8.2 to 34 mg N/ kg wood during the last 5 years of bioreactor operation. Robertson (2010) compared the effect of using the aged wood chips on nitrate removal rates with the fresh chips in the bioreactor. The 7-year-old media showed a mean NO_3^--N removal rate of 9.1 mg N/ L-d which was 75% of the rate for the 2-year-old media (12.1 mg N/ L-d) and was 40–59% of the rate for the fresh chips (15.4–23.0 mg N/ L-d). It indicated that woodchips loose about 50% of their reactivity during their first year of operation as soluble organic compounds are leached. It generally confirmed the multi-year longevity of wood particle for use in denitrifying bioreactors when long-term maintenance-free applications are desired. In a similar study, Robertson et al. (2008) obtained a mixture of sand and wood particles that has been in continuous operation for 15 years treating nitrate from a septic system plume in Southern Ontario (Long Point site). Denitrification rates for the 15-year-old media were measured in dynamic flow column tests and were compared to rates measured in year 1 using the same reactive mixture. Nitrate removal rates in the 15-year-old media varied with temperature, in the range of 0.22 to 1.1 mg N/L/d at 6 ˚C to 10 ˚C, and 3.5 to 6.0 mg N/L/d at 20 ˚C to 22˚C. The latter rates remained within about 50% of the year 1 rates (10.2 mg N/L/d at 22 ˚C).

In addition, Warneke et al. (2011b) determined dissolved organic carbon leaching, dissolved oxygen, temperature, pH, and concentrations of NO_3^-, NO_2^- and SO_4^{2-}, greenhouse gas production of N_2O, CH_4, CO_2 and C loss in a woodchips denitrification bed. The results showed that NO_3^--N concentrations declined along the bed with total NO_3^--N removal rates of 10.1 kg N/d for the whole bed, and NO_3^--N removal rates increased with temperature. The limiting factor for denitrification process was C availability rather than NO_3^--N. Dissolved oxygen concentrations were above 0.5 mg/L at the inlet, but did not limit NO_3^--N removal. The pH increased steadily from about 6 to 7 along the length of the bed. Dissolved inorganic carbon (CO_2) increased an average of 27.8 mg/L, whereas DOC decreased slightly by about 0.2 mg/L along the length of the bed. The bed surface emitted N_2O-N on average of 1% of the removed NO_3^--N. Dissolved CH_4 concentrations showed no trends along the length of the bed. Sulfate concentrations declined along the length of the bed. Ammonium and NO_2^- concentrations were always very low suggesting that dissimilatory nitrate reduction to ammonium by anammox bacteria was an unlikely mechanism for NO_3^- removal. Bioreactor longevity was estimated from surface emission rates of CO_2 and release of dissolved carbon and suggested that available C can support denitrification for up to 39 years.

1.7. Denitrification bioreactor using agricultural residues

The nitrate removal efficiency of denitrification bioreactors is dependent on the quantity of readily biodegradable carbon that can be utilized by the denitrifying bacteria. However, a major portion of organic carbon derived from wood materials is not easily biodegradable since it typically consists of large amounts of high molecular weight aromatic carbons. These aromatic carbons are generally not easily utilized by denitrifying bacteria and can limit the nitrate removal rates (Feyereisen et al., 2016). Organic carbon media derived from agricultural residues such as corn cobs, corn stover and barley straw have shown the ability to produce high quantities of easily biodegradable carbon and to support high densities of denitrifying microorganisms in bioreactors (Healy et al., 2012). Recent studies also showed that on-farm agricultural resides exhibit better nitrate removal performance than woodchips, especially at low temperatures (Cameron and Schipper, 2010; Feyereisen et al., 2016). The cost of denitrifications bioreactors is also partially driven by the cost of organic sources like woodchips (Christianson et al., 2011). Therefore, the use of on-farm agricultural residues in denitrification bioreactors may improve the bioreactor performance and reduce the installation cost.

1.8 Scope of Research

The overall goal of this research was to conduct laboratory experiments to evaluate internal and external nutrients removal to control algal bloom in eutrophic lakes. The research work is divided into three chapters of this dissertation. Chapter 2 focuses on the laboratory evaluation of phosphorous and cyanobacteria precipitation and sediment capping in eutrophic lake water using alum and natural minerals. Chapter 3 addresses the synergistic effects of polyaluminium chloride and phoslock on phosphate and cyanobacteria removal in eutrophic lakes. Chapter 4 compares the quantity and quality of dissolved organic carbon leached from woodchips and agricultural residues.

In Chapter 2, laboratory experiments were conducted to investigate the effect of natural particle aided alum coagulation on phosphate and chlorophyll α removal efficiency. The selected natural particles included zeolite, calcite, limestone, and sand. The impact of alum doses, particle size and dosages on phosphate and chlorophyll α removal, turbidity settling kinetics, and floc resuspension were evaluated. In addition, long-term column sediment capping and resuspension experiments were conducted to evaluate the effectiveness of capping with natural particles on phosphate release from the sediment after alum coagulation. This work is in preparation to be submitted to the Journal of Environmental Science and Pollution Research.

Chapter 3 presents the effect of PAC coagulation, phoslock flocculation, and combined PAC and phoslock treatment on phosphate, chlorophyll α, DOC and turbidity removal in simulated algal bloom lake water. The effect of PAC and phoslock on turbidity settling kinetics and floc resuspension were evaluated through laboratory jar tests. The impact of varying pH values and dissolved organic carbon concentrations on the treatment efficiency was also determined.

In Chapter 4, the cumulative amount of DOC leached from four different carbon sources in denitrification bioreactors including woodchips, corn cobs, corn stover and barley straw were measured during laboratory leaching experiments. The characterization of leaching DOC was investigated by measuring biochemical oxygen demand, chemical oxygen demand, and specific UV absorbance to identify the biodegradability and hydrophobicity of leaching DOC. Total nitrogen, total phosphorous, nitrate and phosphate were also measured for the leachate. Finally, a DOC leaching kinetic study was conducted in three different temperatures of 10, 20, and 30 ˚C.

CHAPTER 2: Laboratory evaluation of phosphorus and Cyanobacteria precipitation and sediment capping in eutrophic lake water using alum and natural minerals

Abstract

Algal blooms caused by cyanobacterial growth as a result of eutrophication is one of the most important water pollution problems in surface waters. The combined phosphorus precipitation and sediment capping are promising technologies to control harmful algal blooms in eutrophic lakes. The objective of this study was to evaluate the use of natural minerals to enhance the precipitation of phosphorus and cyanobacteria during alum coagulation, and to reduce phosphate release during sediment capping. Laboratory coagulation experiments were conducted on a lake water spiked with Anabaena sp. using alum and four natural minerals (zeolite, calcite, limestone, and sand) to determine the effect of natural minerals on chlorophyll α, phosphate and turbidity removal. Long-term column sediment capping experiments were also conducted using different minerals after alum coagulation to evaluate their effectiveness in reducing phosphate release. The results showed that alum coagulation was able to remove 85-90% of phosphate and chlorophyll α from Anabaena sp. enriched lake water samples. The added natural particles did not substantially affect the removal of phosphate and chlorophyll α during combined alum and particle coagulation. However, natural particles substantially increased the floc settling kinetics during coagulation. The combined treatment with alum and particles also increased the resistance of the sediment to disturbance by mixing. The long-term sediment capping experiments showed that capping with natural minerals substantially reduced the levels of phosphate released from the sediment. The results of this study suggest that natural minerals could be used as effective coagulation aids to facilitate floc settling and prevent floc resuspension during lake water coagulation. Natural minerals could also be used as effective capping materials to reduce phosphate releases from sediment after coagulation treatment.

Keywords: algal blooms, phosphorus, Cyanobacteria, alum coagulation, sediment capping, natural minerals

2.1. Introduction

Cyanobacteria blooms have become a widespread water quality problem in surface waters (Blaha et al., 2009; Teta et al., 2017). Eutrophication is known as one of the major causes for harmful cyanobacteria blooms (Smith et al., 1999; Boujelben et al., 2008; Yang et al., 2014; Yin and Kong, 2015). Cyanobacteria blooms and their decomposition products can lead to undesirable water quality effects including high turbidity, dissolved oxygen deficiency, and the release of cyanotoxins, which pose threats to aquatic ecosystems and public health. (Pan et al., 2006; Paerl and huisman, 2008; Conley et al., 2009; Wu et al., 2011; Pan et al., 2012; Han et al., 2013; Lurling and Oosterhout, 2013).

Phosphorous (P) is generally the limiting nutrient for algae growth, and external source P loading reduction is critical to eutrophication control in eutrophic lakes. However, studies have shown that the lake recovery is a slow process even when the external P loading is substantially reduced. The internal P loading from P-rich sediments is one major factor that is responsible for enhanced eutrophication processes and can delay the lake recovery for years to decades (Sondergaard et al., 2001; Gulati and Van Donk, 2002; Selig, 2003; Berg et al., 2004, Cooke et al., 2005; Welch and Cooke 2005; Yang et al., 2014; Yin and Kong, 2015). Therefore, effective in-lake P loading control methods are necessary to expedite lake recovery processes and achieve long-term lake eutrophication mitigation (Yang et al., 2014).

Several methods have been employed to decrease in-lake phosphorous such as sediment dredging (Peterson, 1982; Cooke et al., 2005; Spears et al., 2013), aeration (Spears et al., 2013), and biological treatment (Sondergaard et al., 2007; Gulati et al., 2008; Jeppesen et al., 2009). While some of these methods have limitations in operating cost and implementation and cannot provide a permanent solution, in-situ sediment capping technology has been developed to control P cycling from the sediment. This technology involves placement of a layer of particulate materials at the sediment-water interface to create a barrier between the sediment and overlaying water. In-situ sediment capping is a promising technology that can stabilize sediment, minimize resuspension, and reduce nutrient release from the sediment (Simpson et al., 2002; Kim et al., 2007; Lin et al., 2011). Several sediment capping materials including calcite, zeolite, and lanthanum-enriched bentonite (phoslock) have been evaluated in laboratory and field scales studies (Lin et al., 2011; Lurling and Oosterhout, 2013).

Direct precipitation of P and algal cells is an effective remedial method that can reduce the lake water P content and mitigate lake algal blooms. Aluminum and iron salts are the common coagulants that have been applied for algal bloom control and P reduction in lakes (Drikas et al., 2001; Cooke et al., 2005; Jurczak et al., 2005; Jiang and Kim, 2008; Moore et al., 2009; Han et al., 2013). Although chemical and physical precipitation can remove total P from the water column, the treatment results in low density flocs and it does not provide a long-term prevention of P release from the sediment due to the resuspension of the precipitated flocs. Moore and Christensen (2009) reported that the total P in Newman Lake in Washington decreased significantly the year following the whole lake alum treatment but then increased over the next two years to the pre-restoration levels. The combined phosphorous precipitation and sediment capping technology is a promising method to control harmful algal blooms in eutrophic lakes. The treatment involves precipitation of dissolved and particulate P from the water column and subsequent capping the flocs and immobilization of any P released from the sediment using reactive materials (Pan et al., 2012; Lurling and Van Oosterhout, 2013).

The objective of this study was to evaluate the effectiveness of phosphorus and cyanobacteria precipitation and sediment capping in a eutrophic lake water using alum and natural minerals. Four natural minerals were used as coagulation aids for lake water treatment in this study including sand, limestone, zeolite, and calcite. Laboratory coagulation experiments were performed to evaluate factors affecting the dissolved P and algal cells precipitation and floc resuspension using alum and natural particles. Long-term column experiments were also conducted to investigate the effectiveness of sediment capping with natural minerals after alum treatment on reducing phosphorus release from sediment.

2.2. Materials and methods

2.2.1. Lake Water Samples and Experimental Materials

The lake water samples for this study were collected from Lake Kampeska, located in Watertown, South Dakota, USA. The characteristics of the lake water samples used this study are shown in Table 1. The lake water had very high phosphorus concentrations, which fall into the category of hypereutrophic conditions. Aluminium sulfate octadecahydrate ($Al_2O_{12}S_3.18H_2O$; 98% purity) obtained from Fisher Scientific (Fairlawn, NJ) was used as coagulant for this study. Alum stock solutions were prepared by dissolving aluminum sulfate into water before the laboratory coagulation experiments. Calcite (97.9% $CaCO_3$), Zeolite, Silica Sand (99.7% SiO_2) and limestone were obtained from GLC Minerals (Green Bay, WI), Bear River Zeolite Co. (Preston, ID), U.S. Silica Company

(Frederick, MD), and Martin Marietta Co. (Fort Dodge, IA), respectively. All these natural particles were purchased as particulate forms and were sieved in the laboratory into desired size ranges before the experiments.

2.2.2. Cyanobacteria strains, maintenance, and culture conditions

Anabaena sp. PCC 7120 (here in referred to as *Anabaena* sp. 7120), a model species for filamentous cyanobacteria, (Bryant, 2006; Rippka et al., 1979) was obtained from the Pasteur Culture Collection of Cyanobacteria (Paris, France). For long-term storage, strains were frozen at -80 °C in 5% v/v methanol. For short term maintenance the cyanobacteria were grown on BG11 agar (1.5% agar) (Allen and Stanier, 1968) at pH 7.1, incubated at room temperature under constant illumination of 24 µmol/ m^2-s, and then stored at room temperature. Light intensity was measured with a Heavy Duty Light Meter with PC Interface (Extech Instruments, Waltham MA, USA). In the experiments described below, cyanobacterial cultures were grown in 40 L photo bioreactors (PBRs). PBR trials were conducted in 40 L transparent fiberglass flat bottom tanks (Solar Components Corp., Manchester, NH, USA) that were sparged from the bottom with a mixture of 95-5% air-CO_2 at a rate of 0.25 L/L/min. The culture medium consisted of 30 L of BG11 and was inoculated with 1.5 L (5%) of an Anabaena sp. 7120 culture that had been grown to mid-log phase. The reactors were incubated until 2 days after stationary phase was reached at room temperature (20-22 °C) under constant illumination of approximately 40 µE/ m^2-s using fluorescent lights. After harvesting the bioreactors, Anabaena solution was centrifuged and washed 3 times with high purity water to remove dissolved nutrients. The concentrated Anabaena stock solutions were stored in 2 liters clear glass bottles in an area with natural light at room temperature.

2.2.3. Experimental procedure

The laboratory experiments for this study were divided into two phases. In Phase 1, coagulation experiments were conducted using a Phipps and Bird 6-position jar tester and 500 mL glass beakers to evaluate natural particle aided coagulation on P and Anabaena sp. precipitation and floc resuspension. All natural particles were sieved into four sizes: 44-75 µm, 75-106 µm, 106-150 µm and 150-210 µm, according to standard sieving procedures. All sieved particles were gently rinsed with deionized water to remove any fine particles on the surface and air-dried at room temperature prior to use. Different amounts of Anabaena sp. stock solutions were dosed into 500 mL lake water samples to reach initial turbidity levels of 20±1 NTU or 50±2 NTU before the coagulation experiments.

The first set of coagulation experiments was conducted with alum alone (0-8 mg Al/L) to determine its treatment efficiency of Anabaena sp. spiked Lake Kampeska water samples at an initial turbidity level of 20±1 NTU. The coagulation tests proceeded with rapid mixing at 250 rpm for 2 min, followed by slow mixing at 30 rpm for 20 min. Then, sedimentation was allowed to occur for 24 h. Samples were taken for the measurement of phosphate, chlorophyll α and nitrate. Based on the results of the first set of alum coagulation experiments, an alum dose of 4 mg Al/L was selected for subsequent coagulation experiments. In the second set of coagulation experiments, alum (4 mg Al/L) and each of the four particles at a size range of 44-75 µm and different doses of 0.2-5 g/L were simultaneously added to the Anabaena sp. spiked lake water samples. Coagulated samples were taken after 24 h sedimentation for the measurement of phosphate and chlorophyll α. In order to evaluate the impact of particle aided coagulation on turbidity settling kinetics, the Anabaena sp. spiked lake water samples (20±1 NTU) were treated with alum (4 mg Al/L) and four different natural particles in four different size ranges (44-210 µm) at a dose of 1 g/L during the third set of coagulation experiments. After completing the rapid and slow mixing, samples were taken from 1 cm below the water surface at 1, 2, 5, 10, 30 and 120 min of settling to measure the turbidity. During the fourth set of coagulation experiments, the Anabaena sp. spiked lake water samples (20±1 NTU) were treated with alum (4 mg Al/L) and zeolite (44-75 µm) at different doses (0.2-5 g/L) to determine the impact of particle doses on turbidity settling kinetics. The Lake Kampeska water samples were also spiked with a high level of Anabaena sp. (50±2 NTU) and treated with alum and four different particles (44-75 µm) at a dose of 1 g/L to determine the turbidity settling kinetics. The last set of coagulation experiments was conducted to evaluate the impact of particle aided coagulation on floc resuspension. The Anabaena sp. spiked lake water samples (20±1 NTU) were treated with alum alone or alum with zeolite (44-75 µm and 1 g/L). After 24 h settling, the treated samples were stirred at different speeds (5-250 rpm) for 5 min, and water samples were taken 1 cm below the surface to measure chlorophyll α concentrations. The treated samples were also fully mixed at 250 rpm for 5 min followed by turbidity settling kinetics analysis. This resuspension experiment was conducted 4 successive times for the same sample to evaluate the impact of successive resuspension on turbidity settling. All jar coagulation experiments were conducted in duplicate.

In Phase 2 experiments of this study, laboratory column experiments were used to evaluate the impact of particles aided coagulation on turbidity settling kinetic and to determine the effect of particle capping on phosphate release from the sediment. Two types of acrylic columns were constructed for the two sets of column experiments. Turbidity settling kinetic experiments were conducted in 8.9-cm diameter and 33-cm deep acrylic columns. Water sampling ports were placed at 7 cm (top sample port), 14 cm (middle sample port), and 21 cm (bottom sample port) below the water surface with a headspace of 5 cm. Lake Kampeska water samples were added to the columns after being spiked with Anabaena sp. at levels of 20±1 NTU. Alum or alum with limestone (44-75 µm and 1 g/L) were added to the column reactors and mixed by a motor driven mixer (Arrow 1750, 120 VAC 60 Hz) at 250 rpm for 2 min and 30 rpm for 20 min. After that, water sample were taken from the sample ports during sedimentation at 5 to 1440 min for the measurement of turbidity and chlorophyll α. Laboratory clear acrylic column reactors were also built for the long-term sediment incubation experiments. The column reactors had a diameter of 8.9 cm. Each reactor contained 10 cm of sediment collected from Lake Kampeska, 35 cm of lake water and a headspace of 5 cm. Similar columns dimensions were suggested by Pan et al. (2012) and Gibbs and Ozkundakci (2011) for long-term incubation. The column reactors were spiked with Anabaena sp. to achieve an initial NTU of 20±1. Alum coagulation (4 mg Al/L) was conducted on each reactor. After 24 h sedimentation, sand, limestone, and zeolite (0.5-1 mm) were added to the reactors individually to achieve capping layer depth of 1 and 2 cm, respectively. Two control reactors without any capping materials were also used for the experiments. One of the two control reactors only contained the lake water spiked with Anabaena sp. and the other control reactor was treated with alum alone. After the treatment, water samples were taken at 7 cm (bottom port), 17.5 cm (middle port), and 28 cm (top port) above the sediments at different time intervals (10 to 80 days) for phosphate measurement. In order to investigate the effect of capping material size to block the phosphate release, three different sizes of limestone (0.2-0.5, 0.5-1, and 1-2 mm) were used to form 1 cm capping layers after alum treatment, and samples were taken from 10 to 80 days for phosphate measurement. Two column reactors were also used to investigate the impact of long-term sediment resuspension on phosphate release. One reactor was treated with alum alone, and the other was treated with alum followed by capping with limestone (0.5-1 mm size and 1 cm depth). A motor driven mixer was used to mix the sediment at 250 rpm for 5 min of the two column reactors every 10 days and samples were taken from bottom, middle and top ports of each column every 10 days before the mixing to measure the phosphate concentration.

2.2.4. Analytical methods

Chlorophyll α analyzed in duplicate based on the standard method (10200 H. Chlorophyll) (APHA, 2012). The procedure described below was followed. The Glass fiber filters were used to remove cyanobacteria from the water sample and mechanically grinded to extract the chlorophyll α. This was accomplished via grinding tube and pestle using 10 ml 90% acetone solution as a solvent, and then steeped at 4 °C in dark conditions for 4 h. Finally, the chlorophyll α concentration was measured utilizing "Jeffrey and Humphrey's Trichromatic Equations" (Arar, 1997) using the wavelengths of 750, 664, 647 and 630 nm:

$$C_{E,a} = 11.85 \text{ (Abs 664)} – 1.54 \text{ (Abs 647)} – 0.08 \text{ (Abs 630)}$$

where $C_{E,a}$ = concentration (mg/L) of chlorophyll α in the extraction solution,

A UV-visible spectrophotometer (Shimadzu, UV-160/160A, Japan) was used to measure the absorbance of processed samples for chlorophyll α analysis. The analysis of dissolved phosphate and nitrate was carried out in duplicate using a UV-visible spectrophotometer (HACH, DR 4000, USA) based on the standard methods (4500-P-E phosphate, 4500-NO_3^-B Nitrate) (APHA, 2012). A turbidity meter (HACH, 2100P, USA) was used to measure turbidity in duplicate. pH values were measured using pH meter (Orion 290A+, USA). Alkalinity and hardness were measured based on the standard methods (2320-B Alkalinity, 2340-C Hardness) (APHA, 2012).

2.3. Results and discussion

2.3.1. Alum coagulation of Lake Kampeska water

Figure 1 shows the results of alum coagulation of Anabaena spiked Lake Kampeska water. Nitrate was not amenable to removal by alum coagulation in the dose range of 0 to 8 mg Al/L. Phosphate removal in the lake water was strongly affected by the alum dosage. The theoretical mass ratio of aluminum (Al) and phosphate to form $AlPO_4$ precipitate is 1:3.5. Therefore, it is expected that a minimum of 0.61 mg Al/L would be required to precipitate the phosphate (2.14 mg/L) in the Lake Kampeska water. Certainly, alum coagulation of phosphate in the lake water is a complexed process involving alum, phosphate, particles, organic matter, and other compounds to form a variety of solid phosphate species through precipitation, complexation and adsorption reactions. As shown in Figure 1, the phosphate removal efficiency by alum gradually increased to 31.3% when increasing the dose from 0 to 2 mg Al/L. It is likely that the competition for alum from other compounds including silica particles, algal cells, and organic matter limited the phosphate precipitation efficiency in this alum dose range. The phosphate removal efficiency substantially increased to 77.9% when increasing alum dose to 4 mg Al/L, and only moderate increases in phosphate removal (up to 91.1%) were observed when further increasing the dose to 8 mg Al/L.

Some of the Anabaena cells in the Lake Kampeska water were able to settle without alum coagulation after 24 hours, which led to a 54.3% removal of chlorophyll α. This indicates that this filamentous cyanobacterium has poor settleability in the lake water and a major portion of the Anabaena cells is expected to remain suspended during an algal bloom event. As seen with phosphate removal, only moderate increases in chlorophyll α removal (68.6%) was observed when increasing alum dose from 0 to 2 mg Al/L. However, the removal of chlorophyll α increased to 89.3% at an alum dose of 4 mg Al/L and remained stable when further increasing the dose to 8 mg Al/L. Charge neutralization and sweep coagulation are likely the two major mechanisms responsible for Anabaena removal during coagulation. It is clear that the efficacy of these two mechanisms were limited when the alum dose was below 2 mg Al/L, and peaked at doses above 4 mg Al/L. The results of this coagulation experiment suggest that alum coagulation is an effective treatment technology for removing phosphate and Anabaena from Lake Kempaska water. An alum dose of 4 mg/L was selected for subsequent experiments based on the results shown in Figure 1. Although higher alum doses removed more phosphate, they may also lead to higher dissolved aluminum after coagulation which could increase the risk to aquatic plants and animals due to the toxicity of aluminum.

2.3.2. Effect of particle dosage and size on particle aided coagulation

Particle dosage and size are important parameters that can affect the efficiency of particle aided coagulation for lake water treatment. Different doses (0-5 g/L) of the selected four natural particles (44-75 μm) were added to the Anabaena spiked Lake Kampeska water samples during alum coagulation to evaluate their impact on phosphate and chlorophyll α removal. The results shown in Table 2 suggests that the added particles had limited impact on chlorophyll α removal since the differences in the removal percentages after the treatment were less than 5% for different particle doses. Natural particles and local soils have been evaluated for their ability for algal removal in fresh waters (Pan et al., 2006; Jiang and Kim, 2008). Several particles have shown high efficiency to flocculate algal cells due to the netting and bridging effect (Pan et al., 2006). However, the enhanced coagulation effects due to the added particles were not observed during this experiment. This may be due to the fact that alum coagulation alone was already highly effective in removing Anabaena from the lake water, and adding natural particles did not enhance chlorophyll α removal after 24 h sedimentation. The added particles did not largely interfere with phosphate removal by alum when the particle doses were less than 1 g/L. However, the phosphate removal gradually decreased when further increasing the particle dose to 5 g/L. At this particle dose, the phosphate removal decreased by 3.9 (sand) to 15.4 (zeolite) percentage points compared to alum alone. The reduced phosphate removal at high particle doses may have been caused by competitive consumption of alum by particles which reduced the available amounts for phosphate precipitation.

Although the added particles did not affect the chlorophyll α removal after 24 h sedimentation, they did affect the particle settling kinetics. Figure 2 presents the turbidity levels at different settling times after alum coagulation with particles in different size ranges (44-210 μm) and at a fixed dose of 1 g/L. Alum coagulation of the Anabaena spiked Lake Kampeska water exhibited an initial fast floc settling kinetics during the first 5 min of sedimentation. The turbidity decreased to about 6-8 NTU at 5 min. After that the floc settling kinetics slowed and the turbidity gradually decreased to about 2-3 NTU after 30 min. Particles aided coagulation generally enhanced the floc settling kinetics compared to alum alone. However, only low to moderate increases in turbidity removal at different time intervals were observed when particle sizes were higher than 75 μm. It was visually observed during the coagulation experiments that particles higher than 75 μm quickly settled to the beaker bottom without much interaction with algal flocs during the sedimentation stage. The turbidity removal substantially increased when the particles in the size range of 44-75 μm were used. The turbidity levels of samples treated with alum and natural particles in this size range decreased to 6-10 NTU after 1 minute of sedimentation. These turbidity levels were 50-70% less than those of alum alone, suggesting that the added particles substantially enhance the floc settling kinetics after alum coagulation. The turbidity levels of treated with alum alone and alum with particle gradually approached to each other after 30 min of sedimentation.

The influence of particle dosage of zeolite on turbidity removal is shown in Figure 3 (a). Compared to the alum alone, the added particles at different dosages (0.2-5 g/L) all enhanced the floc settling after coagulation. The optimum zeolite dose was determined to be 1 g/L because this dose resulted the lowest turbidity levels within 1-5 minutes of the settling period. When further increasing zeolite dosage to 5 g/L, the performance of the floc settling reduced. This may be attributed to the increased turbidity caused by zeolite itself at the highest dosage.

Particle aided coagulation also enhanced floc settling kinetics when the Lake Kampeska water sample were spiked with high concentration of Anabaena to reach initial turbidity levels of 50±2 NTU (Figure 3 (b)). This indicates that particles assisted coagulation can help the settling of the cyanobacteria and flocs for a wide range of initial cyanobacteria concentrations. Different particles had similar impact on turbidity reduction. The turbidity levels of the treated samples with particles quickly decreased to 6.3-9.5 NTU after 1 minute of settling. The increased floc settling kinetics of particle aided coagulation may be attributed to increased floc sizes and densities. It is possible that negative charged particles absorb hydrolyzing species of alum resulting in the positive patches, which in turn can adsorb more particles and precipitate (Wu et al., 2009). The algal cells-particle, algal cells-precipitate and precipitate-precipitate collisions occurred during particle aided coagulation may have led to larger and denser flocs which resulted in faster floc settling kinetics. Ghanem et al. (2007) also proposed that particles can hit the microflocs and enter into the floc matrix causing a reduction of the amount of water present in the floc. During slow mixing, these microflocs aggregate to form larger ballasted flocs which result in a faster precipitation. Our visual observation of the particle aided coagulation and flocculation processes also indicate that the added particles were able to absorb algal cells and produce dense flocs that settled much faster than alum produced flocs.

2.3.3. Effect of mixing on floc resuspension and settling

As can be seen in Figure 4 (a), coagulated flocs by alum alone were easily disturbed by the stirring at 5 rpm and were fully mixed when the stirring speed increased to 30 rpm. However, the settled flocs with zeolite were much more resistant to the disturbance by the mixing. The chlorophyll concentration started to increase at the mixing speed of 50 rpm and became completely mixed at 100 rpm. This result suggests that particle aided coagulation not only enhanced floc settling kinetics but also increased the resistance of settled floc to resuspension. Figure 4 (b) shows the effect of successive mixing on turbidity settling kinetics. The added particles exhibited the ability to increase turbidity settling after sediment resuspension up to 4 consecutive times. This suggests that particle aided coagulation may provide long-term benefit of increasing floc resistance to disturbances, stabilizing the sediment, and improving the floc settling ability.

2.3.4. Particle aided coagulation column experiments

In order to simulate the lake condition, the turbidity settling kinetic tests were also conducted in the column reactors. Figure 5 (a) presents the turbidity levels at three sampling locations along the column for samples treated with alum alone and alum aided with limestone. Turbidity spikes after 5 minutes of sedimentation at three sampling ports were observed for the column reactor treated with alum and limestone. These high turbidity levels were presumably caused by the limestone particles themselves. Because of this, this column showed higher turbidity values than the alum alone column at each corresponding sampling port after 5 minutes. Such turbidity spikes during the sedimentation were not observed during the beaker experiments. This may be due to the fact that turbidity samples were collected at 1 cm below the surface for the beaker study, whereas the top sampling port of the column experiments was 7 cm below the water surface. Although the added limestone particles resulted in initial high turbidity at 5 minutes, the resulting flocs showed high settling kinetics which led to lower turbidity levels than the alum treated sample after 10 minutes of settling. The three sampling locations of the alum and limestone treated column showed turbidity levels that were 17.8% to 32.8% lower than corresponding locations of the alum treated column. This result confirms the finding from the beaker experiments that particles aided coagulation could improve the floc settling kinetics and increase the sedimentation efficiency of the algal bloom water after the coagulation treatment. After 10 minutes of settling, the turbidity values at different sampling locations of the two columns gradually approached to each other and reached similar levels after 6 hours. The column treated with alum and limestone also showed consistently lower levels of chlorophyll α than the alum alone column for sedimentation between 5 and 360 minutes. The added limestone particles resulted in 18.4% to 66.0% lower chlorophyll α concentrations at the three samples locations than the alum alone column during this sedimentation period. This a strong evidence that the added particles were able to improve the flocculation efficiency of Anabaena cells during alum treatment. The two columns reached similar chlorophyll α levels after 24 hours settling.

2.3.5. Long-term sediment capping experiments

Table 3 shows the phosphate release during the long-term incubation experiment for two capping layers of 1 and 2 cm and three sample ports in water columns. The three sampling locations showed similar phosphate concentrations at each sampling event for all columns during the 80-day incubation. The phosphate concentrations of the control column reactor that contained the lake water spiked with Anabaena sp. reached to about 4 mg/L after 80 days of incubation. This concentration was twice of the ambient concentration of the lake water. This suggests that Anabaena sp decomposed and released phosphate during the long-term incubation. Alum treated control reactor showed elevated phosphate concentrations after 40 days of incubation and reached phosphate concentrations of 1.37-1.42 mg/L after 80 days. Among the column reactors with capping natural particles, sand was the least effective material to prevent phosphate release from the sediment. Elevated phosphate concentrations were observed in the column with sand capping layer of 1 cm after 40 days of incubation and the phosphate reached 0.72-0.74 mg/L after 80 days. A sand capping layer of 2 cm was able to reduce the phosphate release by 39-42% after 80-day incubation compared to 1 cm capping. Lin et al. (2011) also reported reduced phosphate release from the sediments with the increase of the calcite thickness. Zeolite and limestone exhibited much higher capacity in preventing phosphate release from the sediments than sand. The phosphate concentrations in zeolite and limestone capped columns varied between 0.02 and 0.06 mg/L after 80-day incubation. The high phosphate capping efficiency of these two materials can be attributed to their phosphate adsorption potentials.

The impact of particle sizes on phosphate capping is shown in Figure 6. Limestone with the size range of 1-2 mm had a decreased ability to prevent phosphate release from the sediment compared with the size range of 0.5-1mm and 0.2-0.5 mm. This is due to that coarser materials have smaller surface areas and less adsorption sites compared to finer materials. This is consistent with the study by Gibbs and Ozkundakci, (2011). They reported that modified zeolite with the size of <1 mm could adsorb 45% more phosphate than the size of 1-3 mm in the sediment incubation study. In addition to higher phosphate adsorption capacity, capping particles with smaller sizes could also cover the sediment surface area with less materials (Gibbs and Ozkundakci, 2011). However, fine sediment accumulation may have detrimental impact on lake habitat and ecological conditions. Therefore, the selection of particle sizes for sediment capping should consider both capping efficiency and potential impact on lake habitat.

2.3.6. Effect of successive resuspension on phosphate release during column capping experiments

Column experiments were used to evaluate the effect of sediment capping on phosphate release during successive resuspensions. As can be seen in the Figure 7, the concentrations of phosphate of the three sampling locations of column reactor treated with alum steadily increased from 0.15-0.20 mg/L at Day 10 to 0.58-0.66 mg/L at Day 70 after 7 resuspension treatments. In general, the bottom sampling port of this column reactor showed higher phosphate concentrations than the other two ports. It is interesting to note that the maximum phosphate concentration (0.66 mg/L at Day 70) in the overlying water during the column resuspension experiment was much lower than the maximum phosphate concentration (1.42 mg/L at Day 80) during the static column incubation experiment. It was thought that floc resuspension caused by mixing would lead to higher phosphate release due to the disturbance of the floc structure and the sediment-water interface. However, the column resuspension experiments revealed the opposite results. It is possible that sediment mixing resulted in the release of the alum flocs to the overlying water, and adsorption and precipitation reactions between suspended alum floc and phosphate led to overall less phosphate concentrations in the water column compared to the static incubation experiment. Limestone capping was able to maintain stable phosphate concentrations in the water column without apparent phosphate release from the sediment during 10-30 day incubation period despite the extensive sediment resuspensions. After that, the phosphate concentration gradually increased from 0.12-0.13 mg/L at Day 40 to 0.26 mg/L at Day 70. The limestone capping layer showed the ability to suppress 61% of the phosphate released from the column reactor without capping after 7 successive resuspensions. This result indicates that sediment capping with limestone has the ability to maintain the long-term capping performance despite of the extensive sediment disturbance events.

2.4. Conclusions

The objective of this study was to evaluate the use of natural minerals to enhance the precipitation of phosphorus and cyanobacteria during alum coagulation, and to reduce phosphate release during sediment capping. Laboratory coagulation experiments were conducted on a lake water spiked with Anabaena sp. using alum and four natural minerals (zeolite, calcite, limestone, and sand) to determine the effect of natural minerals on chlorophyll α, phosphate and turbidity removal. Long-term column sediment capping experiments were also conducted using different minerals after alum coagulation to evaluate their effectiveness in reducing phosphate release. The results showed that alum coagulation was able to remove 85-90% of phosphate and chlorophyll α from Anabaena sp. enriched lake water samples. The added natural particles did not substantially affect the removal of phosphate and chlorophyll α during combined alum and particle coagulation. However, natural particles substantially increased the floc settling kinetics during coagulation. The combined treatment with alum and particles also increased the resistance of the sediment to disturbance by mixing. The long-term sediment capping experiments showed that capping with natural minerals substantially reduced the levels of phosphate released from the sediment. The results of this study suggest that natural minerals could be used as effective coagulation aids to facilitate floc settling and prevent floc resuspension during lake water coagulation. Natural minerals could also be used as effective capping materials to reduce phosphate releases from sediment after coagulation treatment.

Table 2.1 Characteristics of water samples collected from Lake Kampeska.

Water Quality	June 26, 2015	October 5, 2016
pH	8.5	8.4
Alkalinity	252 mg/L as $CaCO_3$	264 mg/L as $CaCO_3$
Hardness	412 mg/L as $CaCO_3$	424 mg/L as $CaCO_3$
Nitrate	0.20 mg/L	0.21 mg/L
Phosphate	2.14 mg/L	2.60 mg/L
Total Phosphorus (as PO_4^{3-})	2.25 mg/L	2.65 mg/L

Table 2.2 Effect of natural particles on chlorophyll α and phosphate removal during particle aided alum coagulation of Lake Kampeska water.

Alum+Natural Particles	Chlorophyll α Removal (%)	PO_4^{3-} Removal (%)
Alum (4 mg Al/L)	89.5	78.2
Alum + 0.2 g/L Calcite	90.6	78.0
Alum + 0.4 g/L Calcite	90.0	77.5
Alum + 1 g/L Calcite	89.0	76.8
Alum + 2 g/L Calcite	88.0	76.0
Alum + 5 g/L Calcite	88.0	71.4
Alum + 0.2 g/L Zeolite	90.6	75.8
Alum + 0.4 g/L Zeolite	89.5	73.9
Alum + 1 g/L Zeolite	89.1	73.0
Alum + 2 g/L Zeolite	88.4	69.6
Alum + 5 g/L Zeolite	85.6	62.8
Alum + 0.2 g/L Lime stone	89.8	77.1
Alum + 0.4 g/L Lime stone	89.9	78.4
Alum + 1 g/L Lime stone	90.2	76.2
Alum + 2 g/L Lime stone	89.4	70.7
Alum + 5 g/L Lime stone	89.1	71.7
Alum + 0.2 g/L Sand	90.6	78.2
Alum + 0.4 g/L Sand	91.0	77.0
Alum + 1 g/L Sand	90.2	75.2
Alum + 2 g/L Sand	90.0	74.8
Alum + 5 g/L Sand	90.3	74.3

*Experimental conditions: water sample collection date=06/26/15, initial turbidity of Anabaena spiked water=20±1 NTU, particle size 44-75 μm.

Table 2.3 Phosphate release during sediment incubation column experiments.

Particles	Particle Depth (cm)	Sampling Location	Phosphate (mg/L)					
			Time (day)					
			10	20	30	40	60	80
Lake water		Top	1.75	1.90	2.25	3.00	3.70	3.90
		Middle	1.75	1.90	2.28	3.08	3.75	3.95
		Bottom	1.76	2.01	2.35	3.10	3.77	4.00
Lake water +Alum		Top	0.06	0.06	0.08	0.09	0.60	1.37
		Middle	0.07	0.08	0.08	0.11	0.63	1.40
		Bottom	0.12	0.12	0.12	0.14	0.66	1.42
Zeolite	1	Top	0.03	0.03	0.03	0.04	0.04	0.04
		Middle	0.04	0.04	0.04	0.04	0.04	0.04
		Bottom	0.04	0.04	0.04	0.05	0.05	0.05
	2	Top	0.02	0.02	0.02	0.02	0.02	0.02
		Middle	0.02	0.02	0.02	0.03	0.03	0.03
		Bottom	0.03	0.03	0.03	0.03	0.03	0.03
Limestone	1	Top	0.03	0.03	0.03	0.04	0.04	0.04
		Middle	0.05	0.05	0.05	0.05	0.05	0.05
		Bottom	0.06	0.06	0.06	0.06	0.06	0.06
	2	Top	0.03	0.03	0.03	0.03	0.03	0.03
		Middle	0.03	0.03	0.03	0.03	0.03	0.03
		Bottom	0.04	0.04	0.04	0.04	0.04	0.04
Sand	1	Top	0.08	0.08	0.08	0.34	0.53	0.72
		Middle	0.08	0.08	0.08	0.34	0.54	0.73
		Bottom	0.10	0.10	0.10	0.35	0.55	0.74
	2	Top	0.05	0.05	0.05	0.08	0.11	0.42
		Middle	0.07	0.07	0.07	0.09	0.11	0.43
		Bottom	0.07	0.08	0.08	0.10	0.13	0.45

*Experimental conditions: water sample collection date=10/05/16, initial turbidity of Anabaena spiked water=20±1 NTU, alum dose= 4 mg Al/L, capping particle size= 0.5-1 mm.

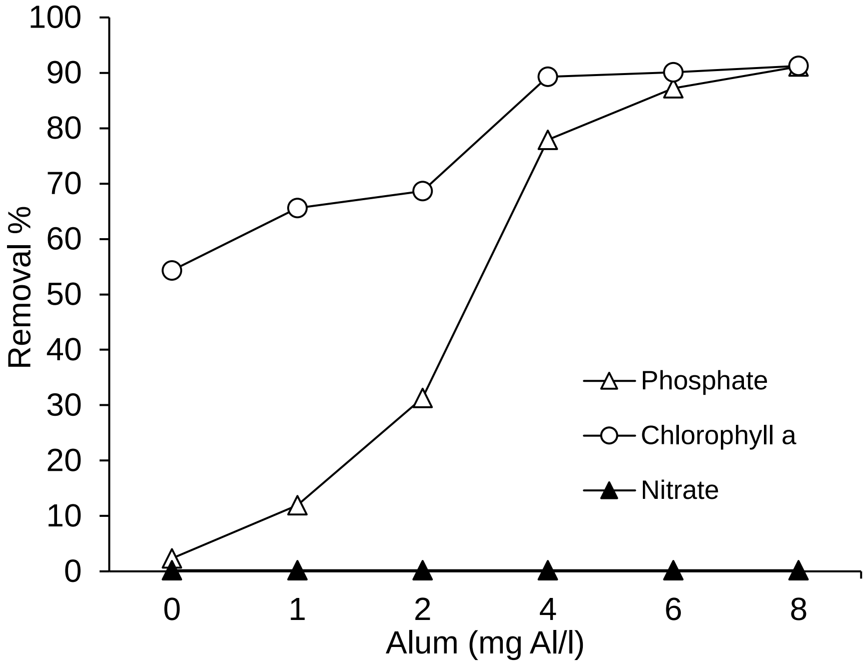


Figure 2.1 Alum coagulation of Anabaena spiked Lake Kampeska water (Experimental conditions: sample collection date=06/26/15, initial chlorophyll α = 500 μg/L)

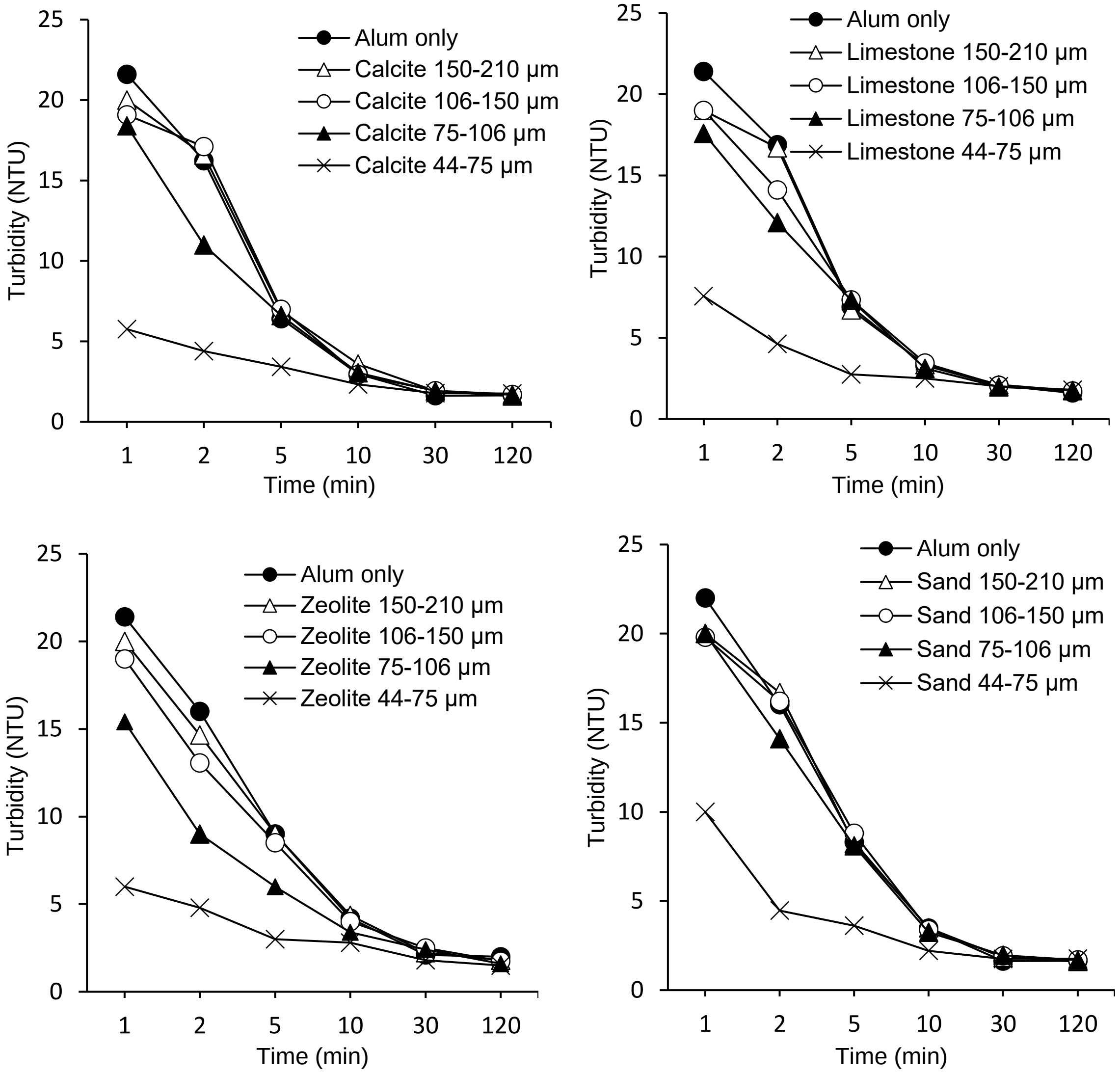


Figure 2.2 Effect of particle sizes on turbidity removal during natural particle aided alum coagulation of Lake Kampeska water (Experimental conditions: water sample collection date=06/26/15, initial turbidity of anabaena spiked water=20±1 NTU, alum dose=4 mg Al/L, particle dose=1 g/L.)

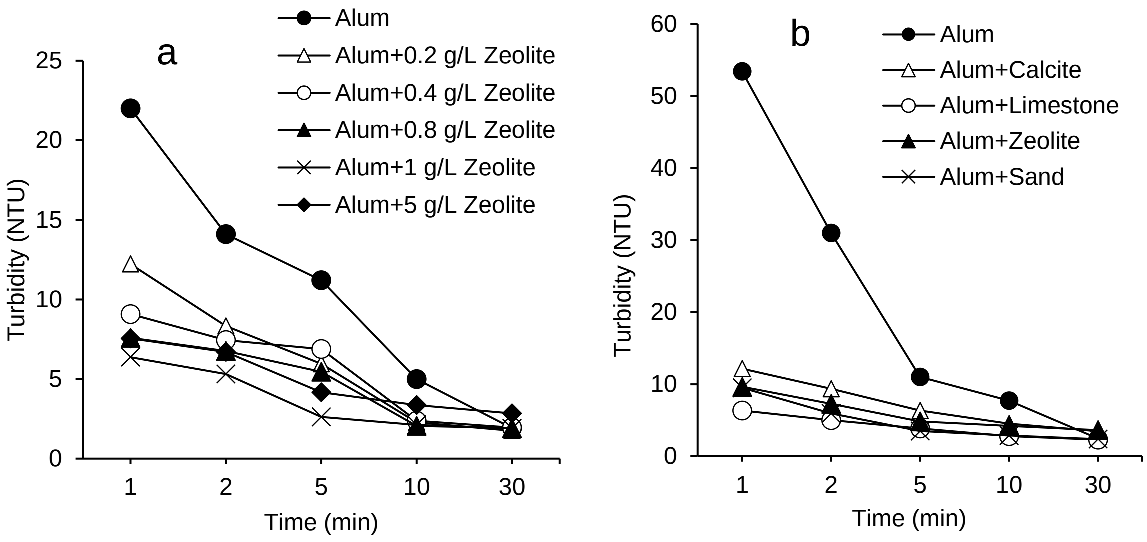


Figure 2.3 Effect of particle dosages on turbidity removal during natural particle aided alum coagulation of Anabaena spiked Lake Kampeska water (Experimental conditions: water sample collection date=06/26/15; (a) initial turbidity=20±1 NTU, alum dose=4 mg Al/L, zeolite size=44-75 µm; (b) initial turbidity=50±2 NTU, alum dose=4 mg Al/L, particle dose=1 g/L, particle size=44-75 µm.)

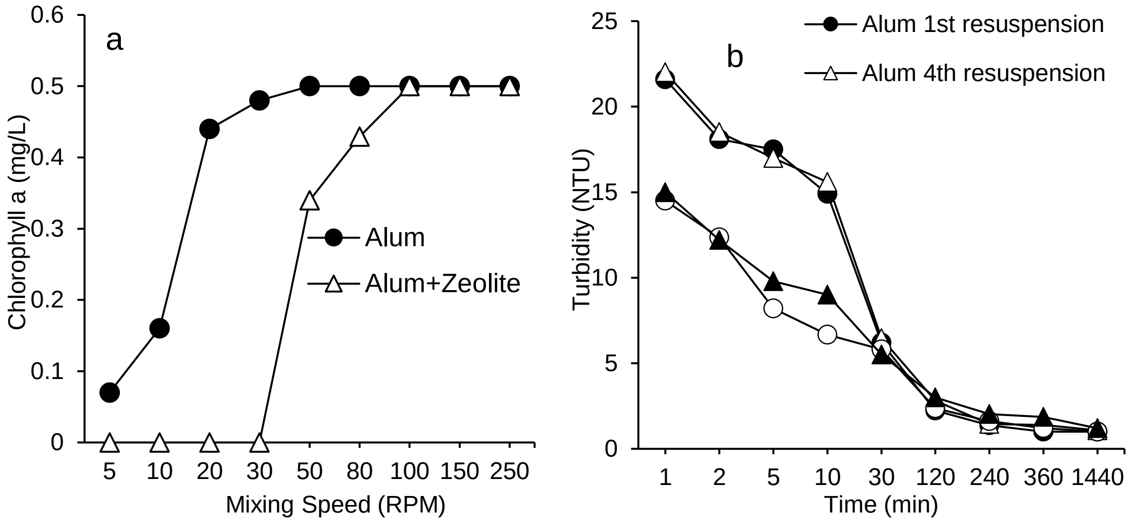


Figure 2.4 Effect of mixing on Anabaena resuspension (a) and turbidity settling kinetics (b) (Experimental conditions: water sample collection date=06/26/15; (a) alum dosage 4 mg Al/L, zeolite dosage 1 g/L, zeolite size 44-75 µm, coagulation settling time before mixing=24 h; (b) resuspension mixing=250 rpm, mixing duration=5 min, time between resuspensions=24 h)

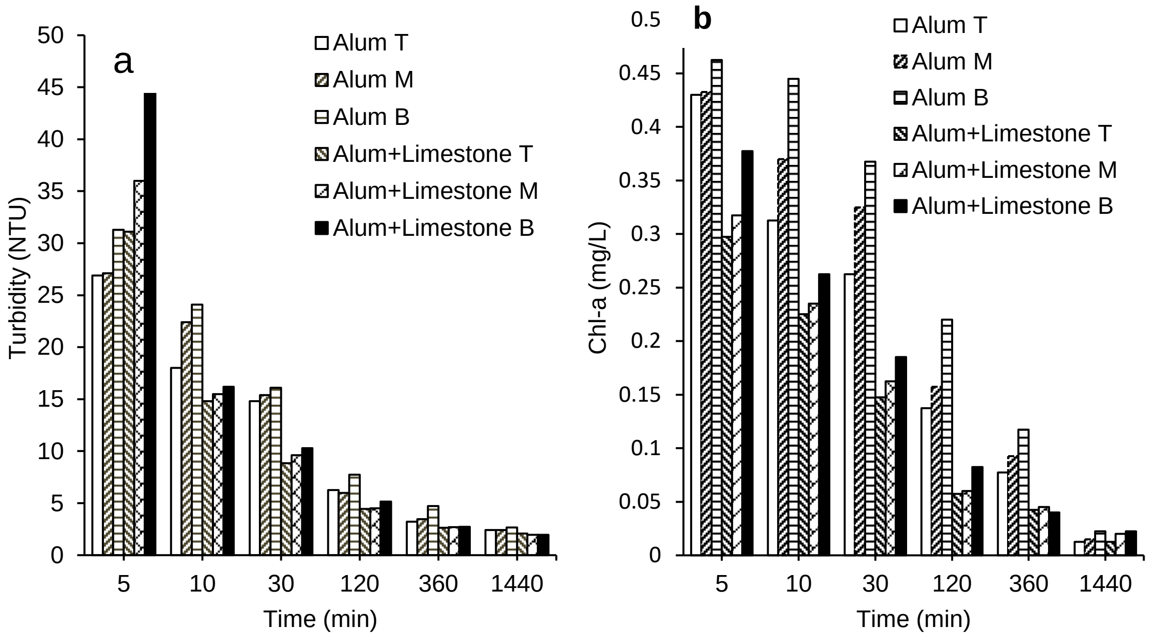


Figure 2.5 Effect of particle aided coagulation on turbidity and chlorophyll α **removal kinetics during column experiments** (T: top sample port, M: middle sampling port, B: bottom sample port; Experimental conditions: water sample collection date=10/05/16, initial turbidity of Anabaena spiked water=20±1 NTU, alum dose=4 mg Al/L, limestone dose=1 g/L, limestone size=44-75 µm.)

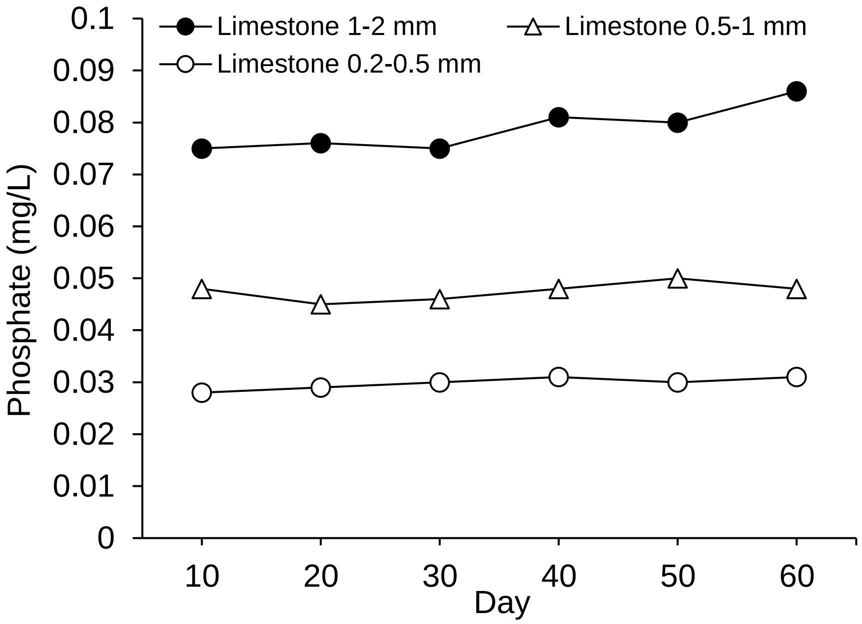


Figure 2.6 Effect of particle size on phosphate release during sediment capping experiments (Experimental conditions: water and sediment sample collection date=10/05/16, initial turbidity of Anabaena spiked water=20±1 NTU, alum dose=4 mg Al/L, limestone capping depth=1cm.)

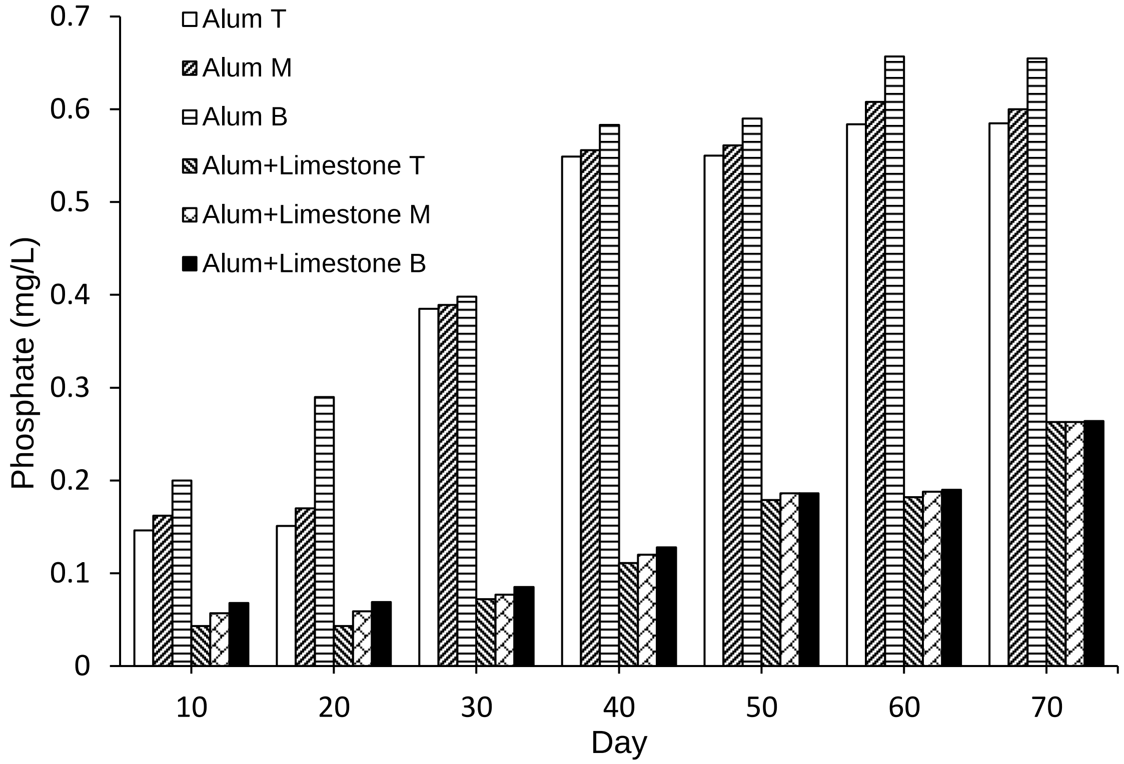


Figure 2.7 Effect of sediment capping on phosphate release during successive resuspension column experiment (T: top sample port, M: middle sampling port, B: bottom sample port; Experimental conditions: water sample collection date=10/05/16, initial turbidity of Anabaena spiked water=20±1 NTU, alum dose=4 mg Al/L, limestone capping depth=1cm, resuspension=250 rpm, 5 min, every 10 days.)

CHAPTER 3: Synergistic effects of polyaluminum chloride and phoslock on phosphate and cyanobacteria removal during coagulation of eutrophic lake water

Abstract

Eutrophication is one of the most widespread water quality problems in lakes and reservoirs. Frequent cyanobacterial blooms resulting from eutrophication can greatly damage aquatic ecosystems and pose a high risk to human health. Polyaluminium chloride (PAC) coagulation and phoslock flocculation are two emerging technologies that have been proposed to reduce phosphorus levels and prevent harmful algal blooms in lakes. The objective of this study was to evaluate the synergistic effects of polyaluminium chloride and phoslock on phosphate and cyanobacteria removal during coagulation of eutrophic lake water.

The lake water samples collected from Lake Kampeska located in Watertown, South Dakota were used as raw water samples for the laboratory coagulation experiments. Anabaena sp., a model species for filamentous cyanobacteria was used to spike the lake water to simulate algal blooms. The lake water samples were treated with PAC, phoslock, and the combination of these two technologies to evaluate their removal efficiencies for phosphate, chlorophyll α, and dissolved organic carbon (DOC). The impact of doses, pH, DOC levels on the removal efficiencies were investigated. The results showed that PAC alone achieved 90% removal for phosphate and chlorophyll α, and 23.6% removal for DOC at the maximum dose of 8 mg Al/L. Phoslock alone removed phosphate, chlorophyll α, and DOC by 70%, 73.3% and 4%, respectively, at a dose of 800 mg/L. The combination of PAC (4 mg Al/L) and phoslock (300 mg/L) resulted in the removal of phosphate, chlorophyll α, and DOC by 90%, 100%, and 35%, respectively, suggesting that the combination of PAC (4 mgAl/L) and phoslock (300 mg/L) is able to significantly enhance the phosphate, chlorophyll α, and DOC removal efficiencies. The combined use of PAC and phoslock exhibited high tolerances to the variations in pH and DOC levels for phosphate and chlorophyll α removal. The combination of PAC and Phoslock also increased the settling kinetics of the flocs. Overall, the results of this study indicate that PAC and phoslock could be used simultaneously to effectively precipitate phosphate and cyanobacteria in lake waters.

Keywords: Polyaluminium chloride, lanthanum-modified bentonite phoslock,
Coagulation process, chlorophyll α removal, Phosphate removal, DOC removal

3.1 Introduction

The fast increase in anthropogenic activities has significantly accelerated the eutrophication process in surface waters (Zamparas and Zacharias, 2014). Phosphorous (P) is the limiting factor in eutrophication condition and can enter to the aquatic ecosystem via different sources such as sewage discharging, and industrial effluents. Extensive use of fertilizers also results in significant concentrations of P in agricultural runoff which enters to the surface waters (Zamparas and Zacharias, 2014).

Cyanobacteria (blue-green algae) bloom is one of the consequences of eutrophication in surface waters. When cyanobacteria blooms begin to die and disintegrate, the water quality is deteriorated by high turbidity, dissolved oxygen deficiency, taste and odor. Also, cyanobacteria blooms can be detrimental for ecosystem and public health since they release potent toxins.

Phosphorous control is critical to eutrophication control. Direct precipitation of P and algae cells is known as an effective restoration technology to reduce the lake water P content and abate algal blooms. Inorganic metal salts such as aluminum and ferric-based salts are the common coagulants that have been used for P reduction and algal bloom control in lakes (Drikas et al., 2001; Cooke et al., 2005; Jurczak et al., 2005; Jiang and Kim, 2008; Moore et al., 2009; Han et al., 2013). Poly aluminum chloride (PAC) as inorganic polymer flocculants attracts a great deal of attentions in recent years since this coagulant contains a range of large hydrolysis and polymeric species which carry a high cationic charge. Using PAC is also beneficent due to the greater size of flocs and better settleability in coagulation process (Sadeghi et al., 2014). A lanthanum-enriched bentonite clay (phoslock) has been also proven to be a strong P binding material in several laboratory and field experiments

(Lurling and Van Oosterhout, 2013; Oosterhout et al., 2014; Noyma et al., 2015). Lanthanum (La) is a rare earth element which has an efficient ratio of 1:1 for La to phosphate (as resulting from $La^{3+} + PO_4^{3-} \rightarrow LaPO_{4(s)}$) when removing P from the water. To prevent any toxic effect of La to the aquatic life, La is infixed into the structure of bentonite clay (Zamparas and Zacharias, 2014). The main purpose of this study was to evaluate the effectiveness of PAC coagulation aided by phoslock flocculation on phosphate, cyanobacteria and DOC removal in eutrophic lake water. The hypothesis for this study is that the combination of PAC and phoslock can decrease the effective dosage of each material for phosphate, cyanobacteria and DOC removal and increase the floc settling kinetics.

3.2 Materials and Methods

3.2.1 Lake Water Samples and Experimental Materials

The lake water samples were collected from Lake Kampeska (located in Watertown, SD), with the area of 21 km^2, shore length of 20 km and the maximum and mean depths of 5 and 2 meters. The characteristics of the lake are shown in Table 1. Polyaluminum chloride (PAC), in three different bacisities of 42, 55, and 70% with 17.1, 10.3, and 10.4% Al_2O_3, respectively, (Kemira company,) were used as coagulant salts. Humic acid salt from Suwannee River obtained by international humic substances society (IHSS) was used in this study. Phoslock was obtained from Sepro company.

3.2.2 Cyanobacteria strains, maintenance, and culture conditions

Anabaena sp. PCC 7120 (here in referred to as *Anabaena* sp. 7120), a model species for filamentous cyanobacteria, (Bryant, 2006; Rippka et al., 1979) was obtained from the

Pasteur Culture Collection of Cyanobacteria (Paris, France). For long-term storage, strains were frozen at -80 °C in 5% v/v methanol. For short term maintenance the cyanobacteria were grown on BG11 agar (1.5% agar) (Allen and Stanier, 1968) at pH 7.1, incubated at room temperature under constant illumination of 24 µmol/ m^2-s, and then stored at room temperature. Light intensity was measured with a Heavy Duty Light Meter with PC Interface (Extech Instruments, Waltham MA, USA).

In the experiments described below, cyanobacterial cultures were grown in 40 L photo bioreactors (PBRs). PBR trials were conducted in 40 L transparent fiberglass flat bottom tanks (Solar Components Corp., Manchester, NH, USA) that were sparged from the bottom with a mixture of 95-5% air-CO_2 at a rate of 0.25 L/L/min. The culture medium consisted of 30 L of BG11 and was inoculated with 1.5 L (5%) of an *Anabaena* sp. 7120 culture that had been grown to mid-log phase. The reactors were incubated until 2 days after stationary phase was reached at room temperature (20-22 °C) under constant illumination of approximately 40 µE/ m^2-s using fluorescent lights. After harvesting the bioreactors, Anabaena solution was centrifuged and washed 3 times with high purity water to remove dissolved nutrients. The concentrated Anabaena stock solutions were stored in 2 liters clear glass bottles in an area with natural light at room temperature.

3.2.3 Experimental procedure

A conventional jar testing technique was employed for coagulation/flocculation test. A six beakers jar test (Phipps & Bird) was assembled at room temperature. The coagulation experiments were conducted in 500 mL glass beakers and proceeded with rapid mixing at 250 rpm for 2 min, followed by slow mixing at 30 rpm for 20 min. Then, sedimentation was allowed to occur for 24 h. Anabaena7120 was dosed into 500 mL lake water to provide an initial turbidity of 20 NTU to simulate algal blooms. PAC with dosages of 1-8 mg Al/L and different basicities of 42, 55, 70% was applied to the water samples. Samples were taken for the measurement of phosphate, chlorophyll α, DOC and turbidity. In the next step, phoslock with dosages ranging from 100-800 mg/L was added to the cyanobacteria spiked lake water to investigate the phosphate, chlorophyll α, DOC and turbidity removal efficiencies. In order to study and compare the synergistic effects of PAC and phoslock on phosphate, chlorophyll α, DOC and turbidity removal, the phoslock dosage was fixed at 300 mg/L and variable PAC dosages of 1,2, and 4 were applied to the water samples. Then, the PAC dosage was fixed at 4 mg Al/L and different phoslock dosages of 100, 200, and 300 mg/L were utilized in water samples. In settling kinetics study, 4 mg Al/L PAC and 300 mg/L phoslock alone and together were applied to the samples to investigate the effect of PAC and phoslock individually and together for turbidity reduction in various settling time. After completing the flocculation process, samples were taken from 1 cm below the water surface in 1, 2, 5, 10, 30… and 1440 min of settling time to measure the turbidity. In the successive resuspension tests, coagulation with PAC and phoslock individually and together was accomplished and samples left for 24 h sedimentation, then the stirrer was located at ~3 cm above the sediment layer and the samples were stirred with the maximum speed (250 rpm) for 5 minutes and turbidity was measured in 1, 2, 5, 10, 30… and 1440 of settling time. All taken samples were poured back in the beakers and left for another 24 h settlement. This was completed 3 times as the results remained constant after this resuspension.

3.2.4 *Analytical Methods*

Chlorophyll α analyzed in duplicate based on the standard method (10200 H. Chlorophyll) (APHA, 2012). The procedure described below was followed. The Glass fiber filters were used to remove cyanobacteria from the water sample and mechanically grinded to extract the chlorophyll α. This was accomplished via grinding tube and pestle using 10 ml 90% acetone solution as a solvent, and then steeped at 4 °C in dark conditions for 4 h. Finally, the chlorophyll α concentration was measured utilizing “Jeffrey and Humphrey’s Trichromatic Equations” (Arar, 1997) using the wavelengths of 750, 664, 647 and 630 nm:

$$C_{E,a} = 11.85 \text{ (Abs 664)} - 1.54 \text{ (Abs 647)} - 0.08 \text{ (Abs 630)}$$

where $C_{E,a}$ = concentration (mg/L) of chlorophyll α in the extraction solution,

A UV-visible spectrophotometer (Shimadzu, UV-160/160A, Japan) was used to measure the absorbance of processed samples for chlorophyll α analysis. The analysis of dissolved phosphate was carried out in duplicate using a UV-visible spectrophotometer (HACH, DR 4000, USA) based on the standard methods (4500-P-E phosphate) (APHA, 2012). The DOC concentrations were determined in duplicate with a Shimadzu TOC-5000 Analyzer (Shimadzu Corp., Kyoto, Japan). A turbidity meter (HACH, 2100P, USA) was used to measure turbidity in duplicate. pH values were measured using pH meter (Orion 290A+, USA). Alkalinity and hardness were measured based on the standard methods (2320-B Alkalinity, 2340-C Hardness) (APHA, 2012).

3.3 Results and discussion

3.3.1 Effect of PAC and phoslock dosages on phosphate, Chlorophyll α, DOC and turbidity removal

Figure1 shows the effects of PAC doses with different basicities on phosphate, chlorophyll α, DOC and turbidity removal. The phosphate removal gradually increased with increasing PAC doses. The three PACs showed different efficiencies in removing phosphate from lake water. The PAC with 70% basicity showed much higher phosphate removal capacities than PACs with lower basicity (Figure1, a). The phosphate removal percentages were 93.8%, 78% and 29.3% for PACs with basicity of 70%, 55% and 42%, respectively, at the highest dose of 8 mg Al/L. Similar trends were also observed for the removal of chlorophyll α. The chlorophyll α removal gradually increased with increasing PAC doses and the PAC with 70% basicity showed higher chlorophyll α removal capacity than PACs with lower basicity (Figure1, b). However, the differences in chlorophyll α removal among the three PACs were much smaller. As can be seen in Figure 1(c) PAC with 70% basicity removed DOC by 24% at the highest dose of 8 mg Al/L. The lower basicity PAC had lower DOC removal capacities. A maximum DOC removal efficiency of 5% was obtained using 8 mg Al/L with 55% basicity. Figure 1 (d) presents the turbidity removal using different dose of PACs. A 93.5% turbidity removal was achieved at 8 mg Al/L with 70% basicity.

Figure 2 shows the phosphate, chlorophyll α, DOC and turbidity removal by phoslock at different doses. The added phoslock increased the chlorophyll α removal from 40% at the ambient condition to 73.2% at the dose of 800 mg/L. This indicates that phoslock was able to flocculate Anabaena sp. and enhance their sedimentation. The phoslock also showed high phosphate adsorption capacity. The phosphate removal increased near linearly with increasing phoslock doses. A 70.5% removal was observed at the highest dose of 800 mg/L. Phoslock had a negligible impact on DOC removal efficiency. A 4% DOC removal efficiency was achieved using 800 mg/L Phoslock. In addition, Phoslock showed the highest turbidity removal of 90% at the dose of 800 mg/L.

3.3.2 Effect of the combination of PAC and phoslock on phosphate, Chlorophyll α, DOC and turbidity removal

Figure 3 (a,b) shows the phosphate, chlorophyll α, DOC and turbidity removal by combined PAC and phoslock. As can be seen in Figure 3 (a), increasing dosages of PAC in samples with a fixed dosage of 300 mg/L phoslock were more efficient to remove the phosphate, chlorophyll α, and DOC in comparison with the increasing dosages of phoslock in samples with a fixed dosage of 4 mg Al/L PAC (Figure 3, b). Phosphate removal efficiency was substantially enhanced from 33% with 300 mg/L phoslock and no PAC to 88.5% using 300 mg/L phoslock and 4 mg Al/L PAC simultaneously. Likewise, chlorophyll α and DOC removal efficiencies were significantly elevated from 55.4% to 99.4% and 2.77% to 33.8%, respectively. An increasing turbidity removal of 10% was also obtained by combined PAC and phoslock. These results suggested that the combination of PAC (4 mgAl/L) and phoslock (300 mg/L) was able to substantially boost the phosphate, chlorophyll α, DOC and turbidity removal efficiencies. These removal efficiencies improvement may be attributed to the synergistic effects of the high flocculation capacity of PAC and the high phosphate adsorption capacity of phoslock. Wu et al. (2011) studied the feasibility of using diatomite with PAC to influence the algae and NOM removal. They found that PAC itself can reduce the chlorophyll α about 95% for doses greater than 30 mg/L and diatomite alone has no removal efficiency for chlorophyll. However, combining PAC and diatomite achieved more than 96% algae removal at PAC dose of 15 mg/L and diatomite dose of 40 mg/L. Addition of diatomite to PAC also showed the NOM removal enhancement of 8.3-24.4% than that for coagulation by PAC only. They proposed the high porosity, large specific surface area, high chemical stability and crystal structure of diatomite are responsible for adsorption of organic pollutants.

3.3.3 Effect of pH variation on phosphate, Chlorophyll α, and DOC removal

Since algal blooms lead to increase in the pH of lakes, the effect of different pH on chlorophyll, phosphate and DOC removal efficiencies was investigated using PAC and phoslock individually and together. Figure 4 shows the effect of different pH on chlorophyll, phosphate and DOC removal efficiency. As pH increased from 6 to 9, phosphate removal efficiency was significantly reduced from 74.55 to 30.5% using phoslock (Figure 4, a). The reduction may be explained by the mechanism involved in removing P with lanthanum hydroxides ($La(OH)_3$). $La(OH)_3$ is formed above pH 7 and begins to precipitate at pH 8.35 (Dibtseva et al., 2001; Ross et al., 2008). Bidentate binuclear (BB) and bidentate mononuclear (BM) are two inner-sphere complexes of P on surface of $La(OH)_3$ which exist at pH values from 3 to 7, but only the BB surface complex forms at pH 9. The shortest P-La interatomic distance forms by BM at pH between 3 and 7 which leads to increase the P adsorption on the surface of $La(OH)_3$, however, the P-La interatomic distance is longer for BB configuration of P on $La(OH)_3$ at pH 9 which is responsible for P adsorption reduction (Fang et al., 2017). As pH increased from 9 to 11, P removal was substantially enhanced from 30.5% to 93.2% using phoslock. The enhanced sorption of phosphate can be attributed to the presence of Ca in alkaline conditions (since the lake water sample used for this study has a high Ca hardness), leading to the co-precipitation of amorphous $Ca_3(PO_4)_2$. This is in agreement with the study by Fang et al. (2017) that obtained the enhanced sorption of phosphate in the presence of Ca in alkaline conditions (Fang et al., 2017). As can be seen in Figure 4 (b), chlorophyll α removal efficiency was gradually decreased as pH increased from 6 to 9 and significantly increased when pH raised up to 11 using phoslock. Algal cells are removed from the water by the main mechanism of charge neutralization. Formation of insoluble $La(OH)_3$ above pH 7 possibly results in positive charge (La^{3+}) reduction on the phoslock surface. Hence, the chlorophyll α removal efficiency reduced. The increase of chlorophyll α removal efficiency with increasing pH up to 11 is likely due to the presence of an amorphous $Ca_3(PO_4)_2$ phase which leads to precipitate algal cells. The increasing pH up to 9 also decreased chlorophyll α and phosphate removal efficiencies about 10% by using PAC. It can be attributed to the formation of soluble $Al(OH)^{4-}$ above pH 7 which reduces the precipitation of chlorophyll and phosphate by $Al(OH)_3$. Chlorophyll α and phosphate removal efficiencies increased by 10% and 20% while pH was raising up to 11. The formation of $Ca_3(PO_4)_2$ at pH>9 is likely the reason of P and algal cells precipitation, thereby enhancing removal efficiencies. It is clear that the removal of phosphate and chlorophyll α was improved by using PAC and phoslock simultaneously. The combined use of PAC and phoslock also exhibited high tolerances to the variation of pH for chlorophyll α and phosphate removal.

As Figure 4 (c) shows, DOC removal efficiency reduced by increasing pH to 11 using PAC, however, no significant difference was observed in DOC removal efficiency using phoslock. The mechanism involved in DOC removal with PAC is strongly pH dependent. In natural water, DOC (humic substances) is negatively charged and soluble at pH values higher than 4 because of the ionisation of carboxylic groups (Lancine et al., 2008). These negative charges can be neutralized by positively charged aluminium hydrolysis species at pH below 6 results in a reduced solubility and precipitation of a metal-humic complex that can be removed from the water. However, the predominant aluminum species at pH above 7 is $Al(OH)^{4-}$ which is a soluble form. Formation of soluble $Al(OH)^{4-}$ above pH 7 reduces the DOC precipitation.

3.3.4 Effect of increasing DOC dosages on phosphate, Chlorophyll α, and DOC removal

Figure 5 shows the effect of extra DOC dosages on phosphate, chlorophyll and DOC removal efficiency. Figure 5 (a) shows that phosphate removal efficiency with phoslock was increased from 33% to 80% as DOC increased from 0 (contains 6.2 mg/L in lake water) to 50 mg/L. It indicates high amounts of DOC helped the phosphate adsorption on the phoslock. This can be explained by the formation of DOC complexes with phoslock which leads to removal of phosphate by adsorption on the solids. Lurling et al. (2014) and Dithmer et al. (2015) achieved different results in which humic substances interfered with the phosphate removal by the phoslock. They studied the effect of humic substances on phosphate removal by phoslock from the eutrophic water with no algal cells. They reported humic substances reduced the effectiveness of phoslock in removing the phosphate due to the formation of humic substances with La that inhibits the $LaPO_4$ precipitation. They also proposed that in general, humic substances may interfere with all other metal-based solids phase phosphate sorbents due to the formation of humic substances with metals (Lurling et al., 2014). However, based on our results, no reduction observed in PAC performance for removing P. Phosphate removal efficiency was even improved from 76% to 97% as DOC increased from 0 to 10 mg/L by using PAC and remained in a similar trend as higher amounts of DOC were applied. This increase can be justified with the formation of DOC-coagulant complexation which can precipitate P. On the other hand, Figure 5 (b) indicates the increasing DOC reduced the performance of PAC and phoslock to remove chlorophyll α from 76.52% to 41.56% and 55.4% to 5%, respectively. In our case, the presence of DOC can interfere with the chlorophyll α removal by PAC and phoslock in the eutrophic water contains chlorophyll. A suggested mechanism involved with the reduction of chlorophyll α removal by PAC in the presence of DOC is the competition between DOC and chlorophyll α for charge neutralization by Al^{3+} and the precipitation by aluminum hydroxide. Phoslock performance reduction for chlorophyll α removal in the presence of DOC also can be explained by the competition between DOC and chlorophyll α for charge neutralization on the phoslock surface area. The combined use of PAC and phoslock showed the high tolerances to the variation of DOC for chlorophyll α removal as well as enhanced P removal efficiency in the presence of DOC.

Figure 5 (c) showed DOC removal efficiency was enhanced from 20.8% to 47% as DOC increased from 0 (6.2 mg/L in lake water) to 56.2 mg/L using PAC. The SUVA number for lake water was lower than 2, suggesting that the hydrophilic fraction with low-molecular-weight was the main DOC component in the lake which results in a weak removal by coagulation (Matilainen et al., 2010). However, the extra DOC which was added to the samples were measured in a SUVA number between 2-4. It indicated the hydrophobic fraction (humic substances) with medium-molecular-weight that can be better removed by coagulation (Matilainen et al., 2010). Jeong et al. (2014) also concluded that the hydrophobic fraction of NOM was better removed by coagulation in alkaline pH. DOC removal efficiency by phoslock also increased with increasing DOC concentrations.

3.3.5 Settling kinetics

Figure 6 shows the effect of PAC and phoslock on turbidity settling kinetics. The Anabaena sp. spiked lake water showed slow turbidity removal kinetics. The turbidity remained stable during the first 30 min and then gradually decrease to 3.5 NTU after 1440 min. When the water samples were treated with PAC and phoslock individually, the turbidity showed appreciable reduction after 30 min of settling and reached an NTU below 8 after 120 min. Combined use of PAC and phoslock showed a rapid turbidity removal within the first 5 min and then the turbidity reduced to 2 NTU after 120 min. These results suggest that combined PAC and phoslock enhanced the settling of flocs formed during coagulation of Anabaena sp. spiked lake water.

The similar results were obtained by Wu et al. (2011). They found not very dense flocs which tended to float using PAC only. However, the coarse flocs which settled after 10 min of settling time were formed after adding diatomite to PAC, and the turbidity remained below 1.2 NTU after 10 min (Wu et al., 2011). The main mechanism of faster turbidity reduction after adding clays can be explained by inter-particle bridging which results in the improvement of incorporating the algae cells into flocs leading to form settleable flocs of greater density, size and strength (Wu et al., 2011).

3.3.6 Successive resuspension

First, second and third successive resuspension studies (Figure 7) showed the appreciable turbidity reduction using combined PAC and phoslock in comparison with Anabaena sp. spiked lake water without any treatment. After first resuspension, lake water turbidity started to decline (from 28 NTU) after 10 min and reached to 17 NTU in 120 min. However, the combination of PAC and phoslock suppressed the same turbidity after 5 min and achieved 3 NTU in 120 min. In second and third resuspensions, turbidity was reduced about 30% (from 29 to 21 NTU) between 30 and 120 min of the settling time for Anabaena sp. spiked lake water. Whereas PAC and phoslock decreased the turbidity more than 87%

after 5 min of settling time (from 30 NTU) and achieved a NTU below 5 in 120 min. These results proposed that combined PAC and phoslock enhanced the faster settling kinetics of flocs after any turbulence occurs in Anabaena sp. spiked lake water.

3.4 Conclusion

The objective of this study was to evaluate the synergistic effects of polyaluminium chloride and phoslock on phosphate and cyanobacteria removal during coagulation of eutrophic lake water. A lake water spiked with Anabaena sp. was treated with PAC, phoslock, and the combination of these two technologies to evaluate their removal efficiencies for phosphate, chlorophyll α, and dissolved organic carbon (DOC). The results showed the combination of PAC and phoslock effectively removed phosphate, chlorophyll α and DOC at lower doses than PAC or phoslock alone. The combined use of PAC and phoslock exhibited high tolerances to the variations in pH and DOC levels during coagulation. The combination of PAC and Phoslock also increased the settling kinetics of the flocs. The results of this study indicate that PAC and phoslock could be used simultaneously to effectively precipitate phosphate and cyanobacteria in lake waters.

Table 3.1. Characteristics of water samples collected from Lake Kampeska.

Water Quality	October 5, 2016
pH	8.4
Alkalinity	264 mg/L as $CaCO_3$
Hardness	424 mg/L as $CaCO_3$
Nitrate	0.21 mg/L
Phosphate	2.60 mg/L
Total Phosphorus (as PO_4^{3-})	2.65 mg/L
DOC	6.2 mg/L

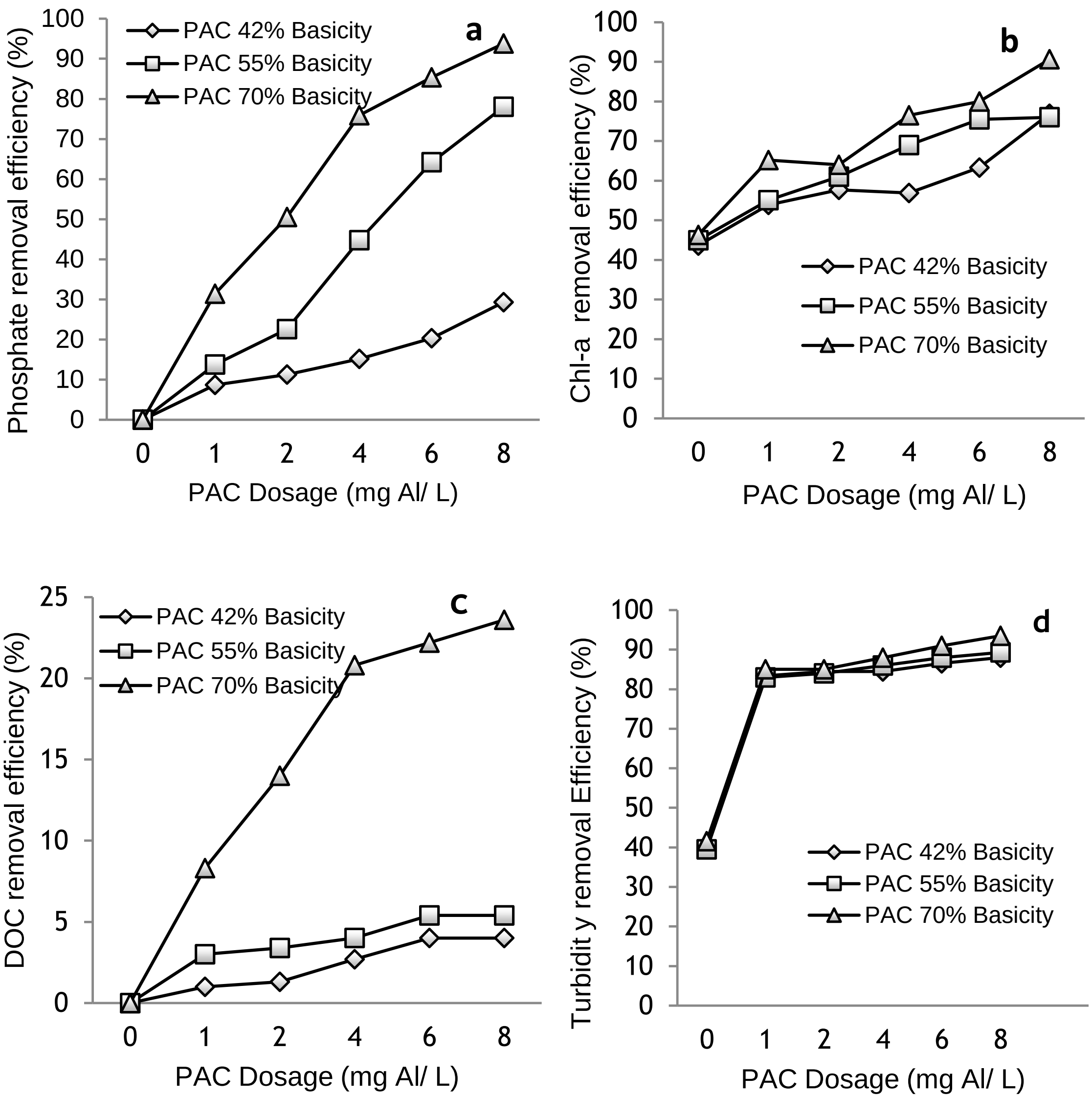


Figure 3.1. Effect of different basicity and dosages of PAC on Phosphate, Chl-a, DOC and turbidity removal.

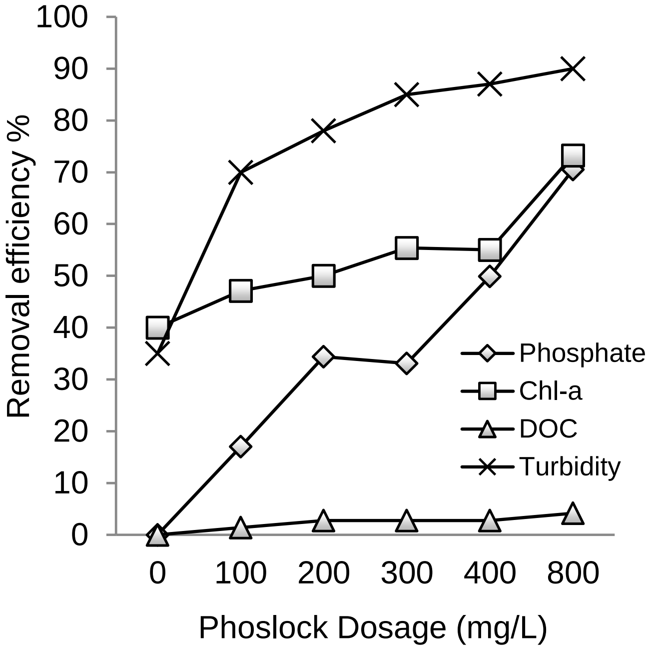


Figure 3.2. **Effect of different phoslock dosages on Chl-a, P, DOC and turbidity removal**

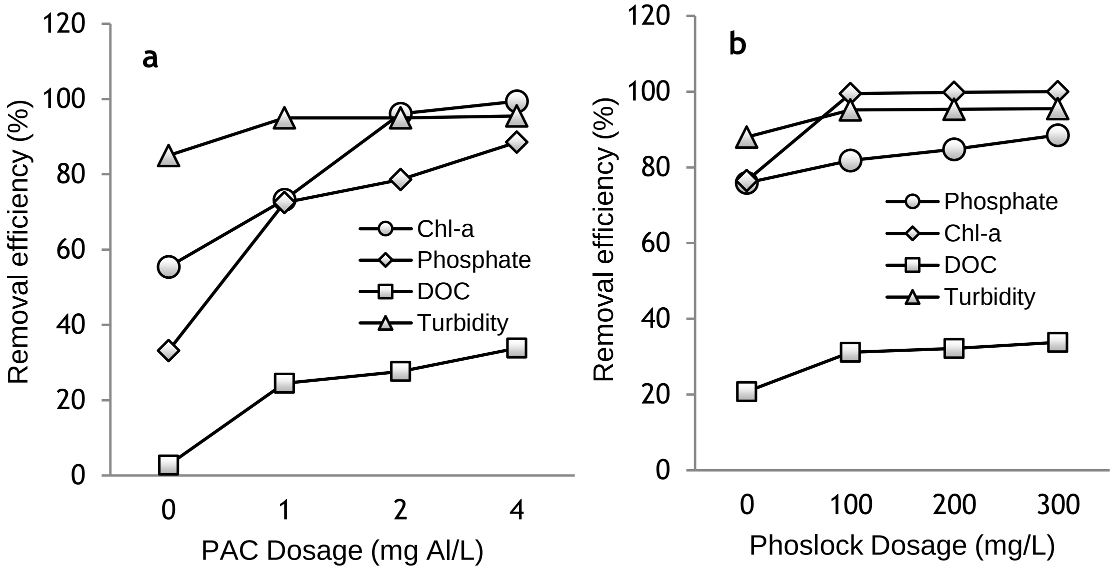


Figure 3.3. **a) Effect of variable PAC dose with fixed phoslock dose of 300 mg/L, b) Effect of variable phoslock dose with fixed PAC dose of 4 mg Al/L on Chl-a, P, DOC and turbidity removal**

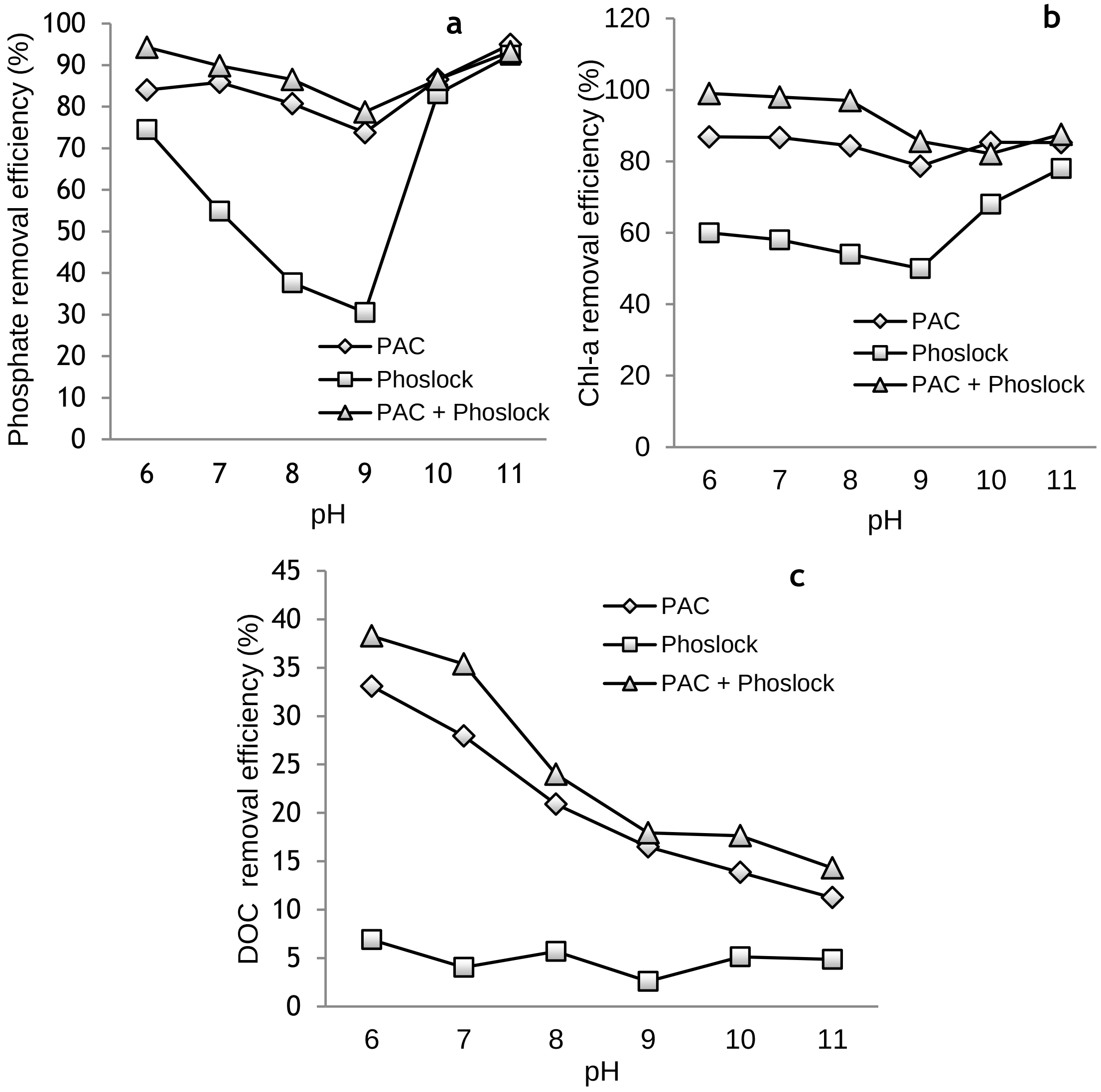


Figure 3.4. **Effect of pH on Chl-a, P, and DOC removal**

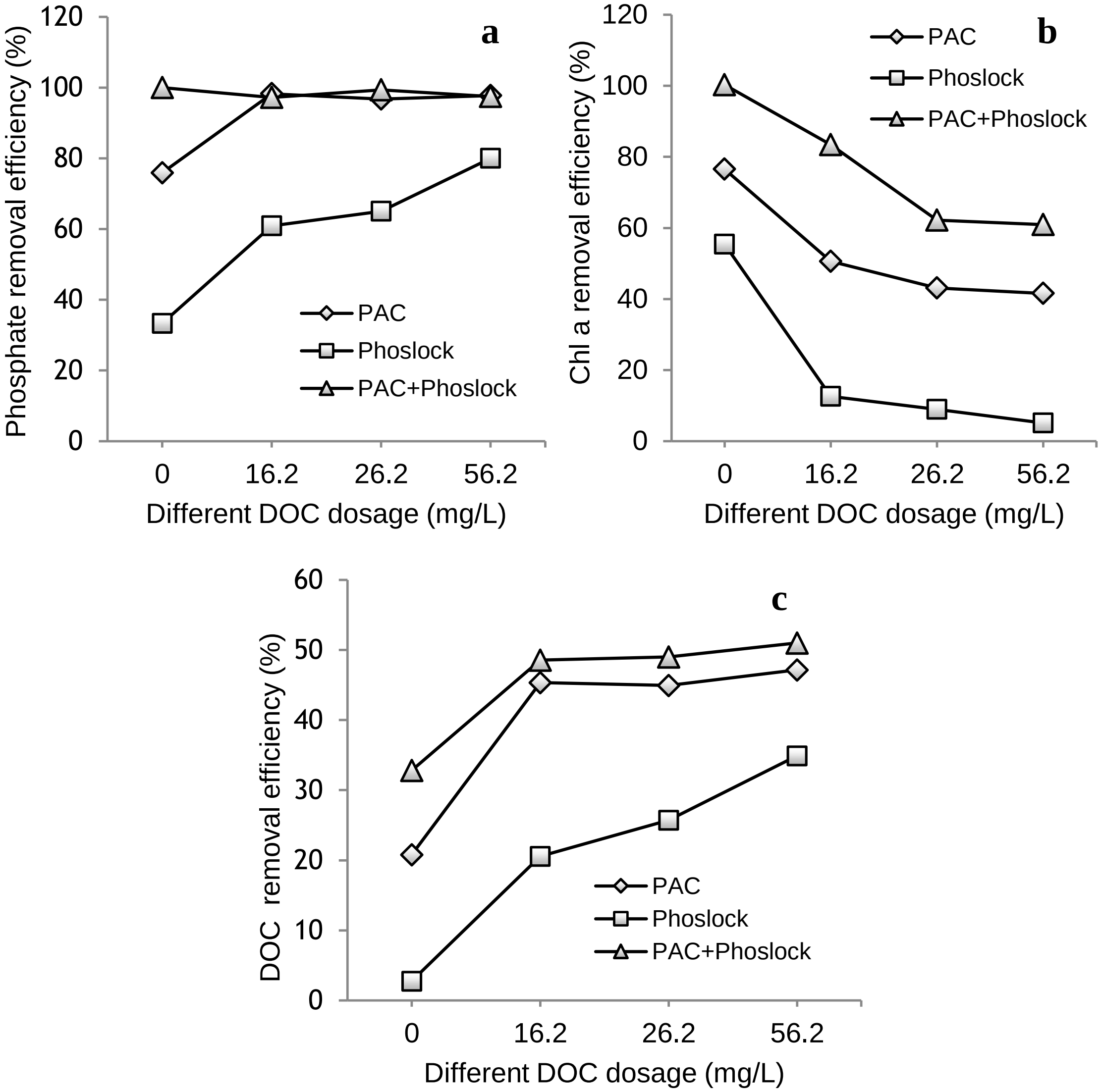


Figure 3.5. Effect of adding DOC on Chl-a, P, and DOC removal

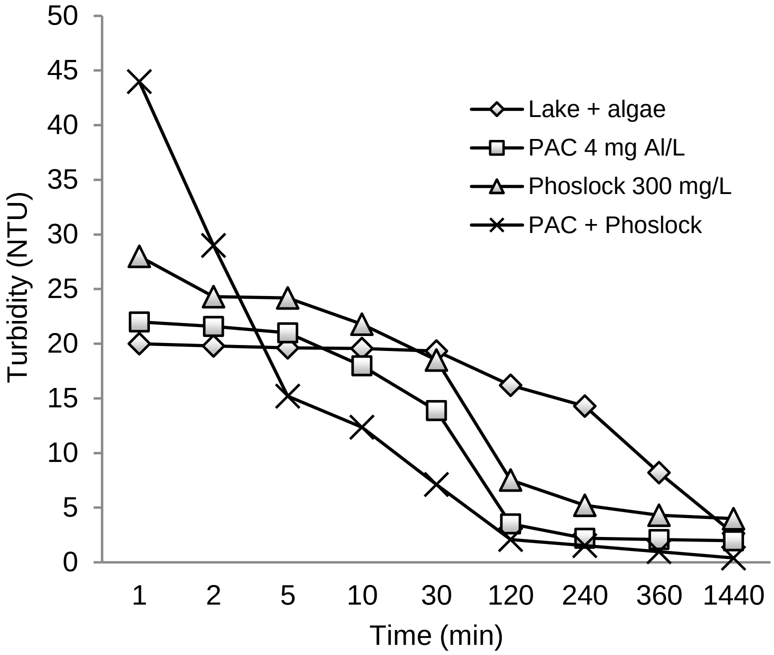


Figure 3.6. Turbidity kinetic study

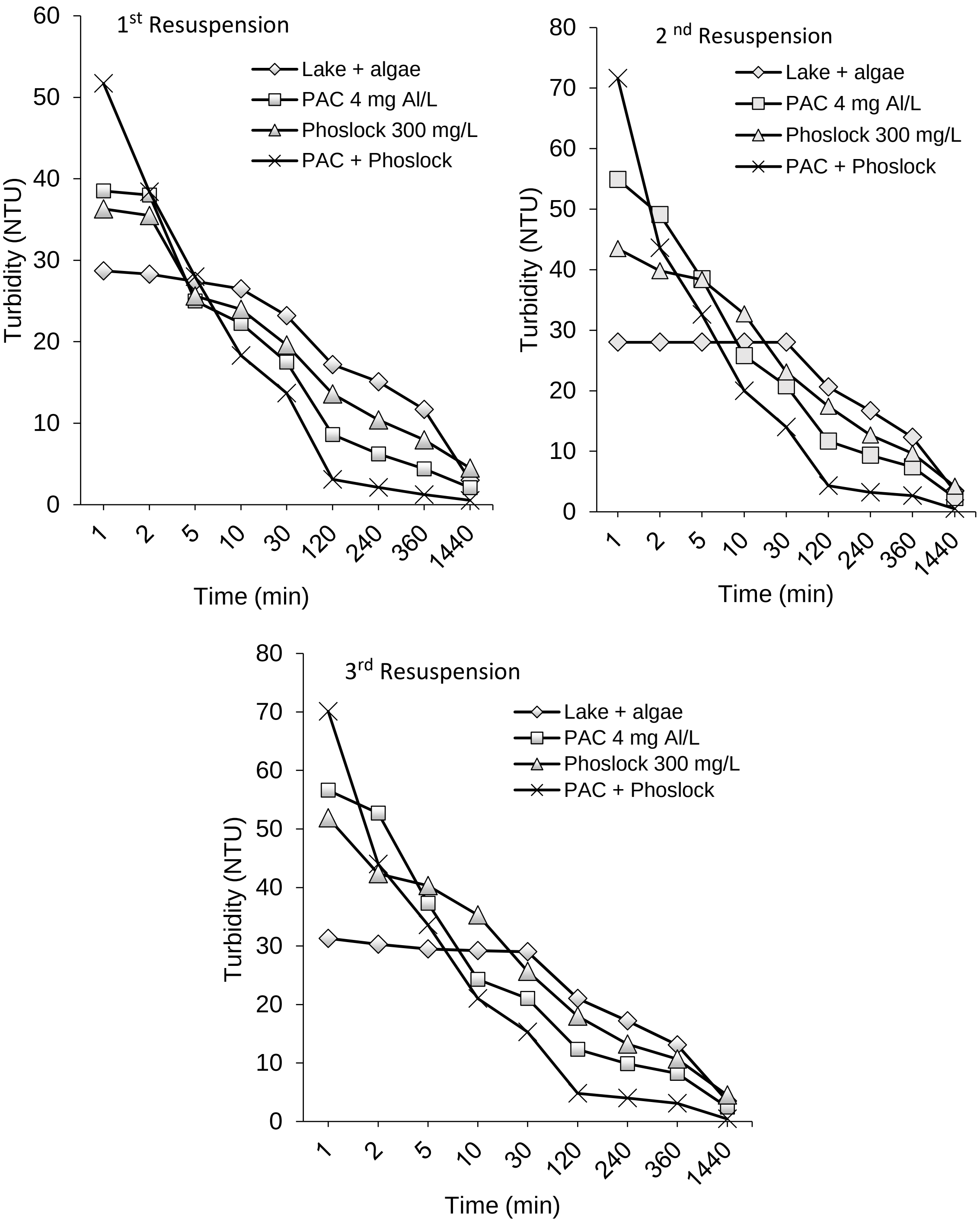


Figure 3.7. Resuspension study

Chapter 4: Evaluation of quantity and quality of DOC leaching from agricultural residues

Abstract

Denitrification bioreactors have been increasingly used to remove nitrate in agricultural subsurface drainage. These bioreactors utilize an organic carbon medium to support the growth of denitrifying bacteria to convert nitrate to nitrogen gas. Woodchips are the most commonly used organic substrate in denitrification bioreactors for subsurface treatment. However, some of the aromatic organic compounds leached from woodchips may not be easily biodegradable which can limit the denitrification efficiency. Organic carbon media derived from agricultural residues such as corn cobs, corn stover and barley straw can produce high quantities of easily biodegradable carbon to support denitrifying microorganisms in bioreactors. The objective of this study was to evaluate the dissolved organic carbon (DOC) leaching characteristics of selected agricultural residues including corn cobs, corn stover and barley straw. The results of this study showed that the DOC leaching potential followed the order of barley straw>corn stover>corn cobs>woodchips. Agricultural residues also exhibited faster DOC leaching kinetics and higher biodegradation potentials than woodchips. Although agricultural residues leached higher concentrations of nutrients during initial flush, those concentrations quickly declined within several days of leaching. The results of this study indicate that organic substrates derived from agricultural residues are well suited for the application of denitrification bioreactors.

4.1 Introduction

Agricultural subsurface drainage is a widely adopted water management practice to increase crop production in the Midwestern United States and many other areas (Fausey et al., 1995). However, nutrients such as Nitrate-nitrogen can be transported from agricultural fields to surface water through subsurface drainage direct conduits (Sims et al., 1998; Jaynes et al., 2001). High nitrate concentration in subsurface drainage water is a major water quality concern. It has been reported that Nitrate-nitrogen concentrations in subsurface drainage water often exceed the United States Environmental Protection Agency (USEPA) drinking water standard of 10 mg/L. The elevated nitrate concentration can lead to eutrophication and harmful algal blooms, hypoxic zones in the ocean, and contamination of drinking water supplies (Rabalais et al., 2002). Therefore, it is necessary to reduce the loss of nutrients through subsurface drainage to protect natural water resources.

Denitrification bioreactors have emerged as an important edge-of-field treatment technology to reduce nitrate loads from subsurface drainage (Blowes et al., 1994; Schipper et al., 2010; Christianson et al., 2011). These bioreactors typically utilize an organic carbon medium like woodchips to support the growth of denitrifying bacteria which reduce nitrate to nitrogen gas (Blowes et al., 1994; Greenan et al., 2006; Robertson, 2010; Cooke and Bell, 2014). The nitrate removal efficiency of denitrification bioreactors is dependent on the quantity of readily biodegradable carbon that can be utilized by the denitrifying bacteria. However, a major portion of organic carbon derived from wood materials is not easily biodegradable, which can limit the nitrate removal rates. It has been reported that organic carbon media derived from agricultural residues such as corn cobs, corn stover and barley straw have the ability to produce high quantities of easily biodegradable carbon and to support high densities of denitrifying microorganisms in bioreactors (Feyereisen et al., 2016; Healy et al., 2012).

The goal of this project is to evaluate the dissolved organic carbon (DOC) leaching potential of agricultural residues in comparison with woodchips, and investigate the DOC leaching characteristics and DOC release kinetics study. The tested materials are corn cobs, corn stover and barley straw. This study is the fundamental research to develop a new bioreactor system that uses a combination of an agricultural residue and woodchips to increase the nitrate removal efficiency and reduce the cost of the bioreactors. The use of on-farm residues may also increase the acceptance of this technology for agricultural water management.

4.2. Materials and Methods

4.2.1 Materials

Corn cobs, corn stover, and barley straw were obtained from SDSU Southeast Research Station near Beresford, South Dakota (SD) and wood chips were collected from a supplier in Sioux Falls, SD. All agricultural residue materials cut in an average range of 2.5-3.5 cm, and the similar size of wood chips was selected from the supply. All materials were washed with Nano pure water to remove dirt and floating fine particles, then dried in 104 ˚C overnight prior to use.

4.2.2 Leaching test

The leaching potential of the materials was determined using a sequential batch leaching procedure. The leaching test was conducted at a ratio of liquid to solid (L/S)

0.9/0.02 L/kg. A 20 g oven dried (104 ˚C) sample of each material were added to a 900 ml Nano pure water (pH 5) and shaken on an orbital shaker at 200 rpm for 24 h. All samples were removed from the shaker and manually inverted two times and immediately filtered with a 0.45 µm filter and stored in refrigerator. This sequential batch leaching procedure was repeated every 24 h until the DOC of the leachate water was below 0.09 mg/g (2 mg/L).

4.2.3 DOC release kinetic study

A DOC release kinetic study was performed in three different temperature of 10, 20, and 30 ˚C for a maximum time of 200 h when the leaching had reached a steady state of DOC release. Samples were taken from all vessels every 2 h, 4 h, 8 h, 24 h, 48 h,..up to 200 h and immediately filtered with a 0.45 µm filter and measured in duplicate for DOC. Several predictive equations such as First-order, Second-order, Elovitch, Fractional Power, and Intra-particle diffusion model have been used to quantify the leachable fraction of an element and its associated release rate constants. The linearized form of the first-order model may be expressed mathematically by equation (4.1):

$$\mathrm{Ln}\ D_t = \mathrm{Ln}\ D_{t0} - k\ t \tag{4.1}$$

where D_t is the cumulative solute released per unit mass of material (mg/g) at time t, D_{t0} is the cumulative solute released per unit mass of material (mg/g) at time 0, t is leaching time in hours and k is the equilibrium rate constant. The constant can be obtained from the slope of the linear plot of Ln D_t versus t. The linearized form of the second-order model is as following:

$$1/\ D_t = 1/\ D_{t0} + k\ t \tag{4.2}$$

The parameters have been defined above. The constant can be obtained from the slope of the linear plot of $1/D_t$ versus t.

The Elovich or Roginsky–Zeldovich equation is generally expressed as follows (Ho and McKay, 2002):

$$d\,Dt/dt = \alpha \exp(-\beta\,Dt) \qquad (4.3)$$

where α and β are fitted parameters. To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha \beta t >> 1$, and on applying the boundary conditions Dt = 0 at t = 0 and Dt = Dt at t = t, equation (4.3) then becomes (Sparks 1986):

$$Dt = \beta \ln(\alpha\beta) + \beta \ln t \qquad (4.4)$$

Thus the constants can be obtained from the slope and intercept of the linear plot of Dt versus Ln t.

The fractional power function model is a modified form of the Freundlich equation and can be expressed by equation (4.5) (Ho and McKay, 2002; McLaughlan and Al-Mashaqbeh, 2009 b) or its linear form as given in equation (4.6):

$$Dt = a\,t^{b} \qquad (4.5)$$

$$\mathrm{Ln}\,Dt = \mathrm{Ln}\,a + b\,\mathrm{Ln}\,t \qquad (4.6)$$

where a (mg/g h) and b (dimensionless) are constants and the constants can be obtained from the slope and intercept of the linear plot of Ln Dt versus Ln t.

The intra-particle diffusion model may be expressed as follows (McLaughlan and Al-Mashaqbeh, 2009 b):

$$Dt = k\, t^{0.5} \tag{4.7}$$

where k (mg/g $h^{0.5}$) is a constant parameter and can be obtained from the slope of the linear plot of Dt versus $t^{0.5}$.

Some assumptions should be considered while using these equations. First, water soluble organic carbon is the only available leaching solution that can be measured. Second, DOC transformation to non-extractable forms should be negligible. Third, the DOC release during the leaching period can be modelled as a net desorption process (McLaughlan and Al-Mashaqbeh, 2009 b).

4.2.4 Analytical methods

All solutions used in this study were prepared with ultrapure water (18MU-cm) produced by a Barnstead Nano pure system. The analysis of total and dissolved phosphate (TP, PO_4^{3-}-P), total nitrogen (TN) and nitrate-nitrogen (NO_3^--N) was carried out in duplicate using UV-visible spectrophotometer (HACH, DR 4000, USA) based on the standard method (4500-P-E Phosphate, 4500-$NO_3^{—}$B Nitrate, 4500-N C Total Nitrogen) (APHA, 2012). The DOC concentrations were measured in duplicate with a Shimadzu TOC-5000 Analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310 B (APHA, 2012). The UV absorbance at 254 nm (UV254) of DOC was measured by a Hach DR4000U spectrophotometer (Hach, Loveland, CO). SUVA (specific ultraviolet absorbance) was calculated from UV254 divided by the DOC. Chemical oxygen demand (COD) and biological oxygen demand (BOD) were determined according to Standard Method 5220 D and 5210 B, respectively (APHA, 2012).

4.3 Results and Discussion

4.3.1 DOC leaching

Figure 1 presents the DOC leached from four materials during the sequential batch test. According to the results, barley straw leached the highest cumulative amount of DOC (29.27 mg/g) among the materials and wood chips has the lowest cumulative leached DOC (5.25 mg/g) after 20 days. The release of DOC was characterized by an initial high release within initial time period (<24 h) for all agricultural residues followed by a rapid decline in DOC values after day 1 and by a slower rate during later time periods. The initial leaching DOC of 20.49 mg/g barley straw, 15.52 mg/g corn stover, and 9.28 mg/g corn cobs in day 1 decreased to 3.30, 3.48, and 3.87 mg/g in day 2, respectively and gradually decreased to <1 mg/g after day 3. Woodchips showed the lowest amount of 1.93 mg/g DOC leached in day 1 decreased to 0.70 mg/g in day 2. All agricultural residues showed the higher amount of leaching DOC than woodchips during the sequential batch test. The results of this test suggest that agricultural residues can produce high quantities of organic carbon and to support denitrifying microorganisms in bioreactors. The results of this study was similar to the previous study by McLaughlan and Al-Mashaqbeh, (2009a) who obtained the high release of DOC from composted garden organics, pine and hard wood materials within the initial time period (<24 h) and followed by a rapid decline afterwards.

DOC leaching characteristics

As shown in the Figure 2 (a), wood chips showed the highest SUVA values among other materials. The highest SUVA values were likely attributed to the hydrophobic and high molecular weight (MW) organic compounds released by woodchips (Abusallout and

Hua, 2017). The hydrophobic natural organic matter is typically rich in aromatic carbon and UV-absorbing compounds (Hua and Reckhow, 2007), and they are hard to be consumed by microorganisms in the degradation process. The SUVA values gradually increased as the percentage of hydrophobic fraction increased with time. The increased hydrophobic fraction with longer operation time agrees with the BOD/COC results shown in Figure 2 (b). As can be seen in the Fig, woodchips has the lowest BOD/COD ratio and the ratio decreased by increasing time. If BOD/ COD is > 0.6 then the waste is fairly biodegradable. If BOD/COD ratio is between 0.3 and 0.6, then the process will be relatively slow. If BOD/COD < 0.3, biodegradation will not proceed (Abdalla and Hammam, 2014). Thus, the reduced BOD/COD ratio with longer operation time indicates the increasing hydrophobic fraction of organic carbon which is not biodegradable by microorganisms. Corn cobs has the highest BOD/COD ratio which is associated with the lowest SUVA values indicating the most biodegradable organic carbon with the lowest hydrophobic fraction. The results of this study suggest that agricultural residues could be the more biodegradable source of organic carbon for microorganism in comparison with wood chips.

4.3.2 Nutrient Leaching

As can be seen in Figure 3, corn stover and barley straw showed the highest amount of nutrient leaching among the materials. They also exhibited fast nutrient depletion rates, and the leaching nutrients substantially decreased in day 2 and gradually reduced to zero after one week. Woodchips showed the least amount of NO_3^--N and TP release among the materials. Corn cobs showed no release of NO_3^--N and much less release of TN, TP and PO_4^{3-}-P than other materials except woodchips which had a lower TP leaching than corn cobs. Corn cobs also exhibited much slower rates of nutrients depletion after day1.

Generally, the leaching nutrient may come from either the soil nutrient accumulation attached to the materials or the nature of agricultural residues. If a relatively large amount of nutrient was present in the residue material, then a greater quantity of nutrient was leached into solution (Cermak et al, 2004). Cermak et al, (2004) investigated the nutrient leaching from corn and wheat residues. They found more PO_4^{3-}-P and NO_3^--N leaching from corn residue than wheat residue after one day contact time. This can be explained by the time that wheat residue collected after harvest. Before it was collected, the wheat residue had been in the field for 119 days after harvest, and thus substantial leaching of nutrients may have already taken place (Cermak et al, 2004).

4.3.3 Kinetic modelling

The DOC release data is presented as cumulative release data for modelling purposes. The various kinetic models parameters were shown in Table 1. The results showed that first and second-order models generally have a poor goodness of fit for all data. This was especially evidenced by the relatively low R^2 (<0.86) for temperature 20 and 30 °C. The three other models showed a general good fit for corn cobs and woodchips by a high R^2 (>0.86) in different temperatures. However, the best fit (>0.95) occurred in temperature 10 °C with intra-particle model for all materials. These results give an insight into the mechanisms controlling the rate of DOC release in intra-particle model. There are three mechanisms involved in DOC release as film diffusion, intra-particle diffusion, and desorption (McLaughlan and Al-Mashaqbeh, 2009 b). While film diffusion is a mass transport across the liquid film surrounding the particle, the internal-particle diffusion is an internal mass transport within the particle boundary. Some researchers reported that initial curved portions of the intra-particle model plot show film diffusion while linear portions suggest intra-particle diffusion (Gerente et al, 2007; McLaughlan and Al-Mashaqbeh, 2009 b). At longer time the rate of release decreased and DOC desorption may control the leaching (McLaughlan and Al-Mashaqbeh, 2009 b). In this study, intra-particle diffusion dominates the leaching process after approximately 24 h. This is evident in the best data fit for a linear trendline (Table 2) when cumulative DOC is plotted versus the squared root of operation time. McLaughlan and Al-Mashaqbeh, (2009 b) obtained the similar results with pine and compost DOC leaching. They found the intra-particle diffusion dominated the leaching process after 22 h.

Effect of temperature on DOC leaching rate

Figure 4 shows that the DOC leaching rate improved as temperature increased. However, the maximum amount of carbon that can be leached from these materials, is independent of temperature. The more rapid leaching rates could represent the readily soluble DOC leached from the materials (McLaughlan and Al-Mashaqbeh, 2009 b). Barley straw and corn stover obtained the maximum release within 150 h, 24 h, and 8 h in 10 °C, 20 °C, and 30 °C, respectively. Corn cobs reached the highest DOC leaching within 168h, 48h, and 24h in 10 °C, 20 °C, and 30 °C, respectively. No significant difference was observed with woodchips in different temperatures. This is in agreement with Whitworth et al, (2014) who investigated the temperature dependence of carbon leaching from a common floodplain litter component in south-eastern Australia. They found that the leaching rate substantially increased with increasing temperature to 30 °C. Whereas, the maximum amount of carbon that can be leached from the leaf material, is independent of temperature (Whitworth et al, 2014). The increasing leaching DOC rate in higher temperatures can be explained by microbial action within or on the surface of the materials that progressively decompose complex carbon compounds into smaller and more soluble forms, thereby, increasing the potential for leaching (Whitworth et al, 2014).

4.4 Conclusion

Woodchips are the most commonly used organic substrate in denitrification bioreactors for subsurface treatment. However, some of the aromatic organic compounds leached from woodchips may not be easily biodegradable which can limit the denitrification efficiency. Organic carbon media derived from agricultural residues such as corn cobs, corn stover and barley straw can produce high quantities of easily biodegradable carbon to support denitrifying microorganisms in bioreactors. The objective of this study was to evaluate the dissolved organic carbon (DOC) leaching characteristics of selected agricultural residues including corn cobs, corn stover and barley straw. The results of this study showed that the DOC leaching potential followed the order of barley straw > corn stover > corn cobs > woodchips. Agricultural residues also exhibited faster DOC leaching kinetics and higher biodegradation potentials than woodchips. Although agricultural residues leached higher concentrations of nutrients during initial flush, those concentrations quickly declined within several days of leaching. The results of this study indicate that organic substrates derived from agricultural residues are well suited for the application of denitrification bioreactors.

Table 4.1. Fitted and measured parameters for the various kinetic model

Parameters	Barley straw			Corn stover			Corn cobs			Woodchips		
	Temperature			Temperature			Temperature			Temperature		
	10	20	30	10	20	30	10	20	30	10	20	30
First-order												
R^2	0.892	0.431	0.339	0.815	0.462	0.554	0.918	0.691	0.713	0.855	0.754	0.858
k	0.004	0.002	0.002	0.006	0.004	0.003	0.008	0.01	0.006	0.007	0.007	0.007
Second-order												
R^2	0.890	0.426	0.328	0.746	0.424	0.505	0.834	0.641	0.682	0.769	0.697	0.781
k	<-0.001	<-0.001	<-0.001	<-0.001	<-0.001	<-0.001	-0.001	-0.001	<-0.001	-0.003	-0.002	-0.003
Power												
R^2	0.928	0.815	0.690	0.966	0.835	0.832	0.930	0.952	0.962	0.963	0.968	0.970
a	449.68	1443.44	1658.06	93.39	281.32	399.94	17.73	21.49	81.24	0.483	2.82	2.16
b	0.159	0.076	0.058	0.266	0.145	0.104	0.310	0.341	0.174	0.311	0.227	0.208
Intra-particle												
R^2	0.960	0.613	0.501	0.976	0.668	0.725	0.972	0.876	0.882	0.978	0.930	0.962
k	1.482	0.791	0.627	1.687	0.890	0.741	1.241	1.406	0.815	0.240	0.280	0.235
Elovich												
R^2	0.891	0.816	0.706	0.950	0.861	0.860	0.865	0.945	0.963	0.912	0.977	0.971
β	3.826	2.164	1.635	4.483	2.396	1.773	3.125	3.464	1.870	0.653	0.682	0.519
α	386	3*10^10	10^15	1.65	19514	2*10^7	0.496	0.78	950	2.49	91	311

Table 4.2. Intra-particle model parameters.

Materials	Regression Equation of trendline	R^2
Corn Stover	Y=1.52x + 6.64	0.966
Barley straw	Y=1.33x + 13.33	0.960
Corncobs	Y=1.12x + 2.29	0.972
woodchips	Y= 0.22 x + 0.58	0.978

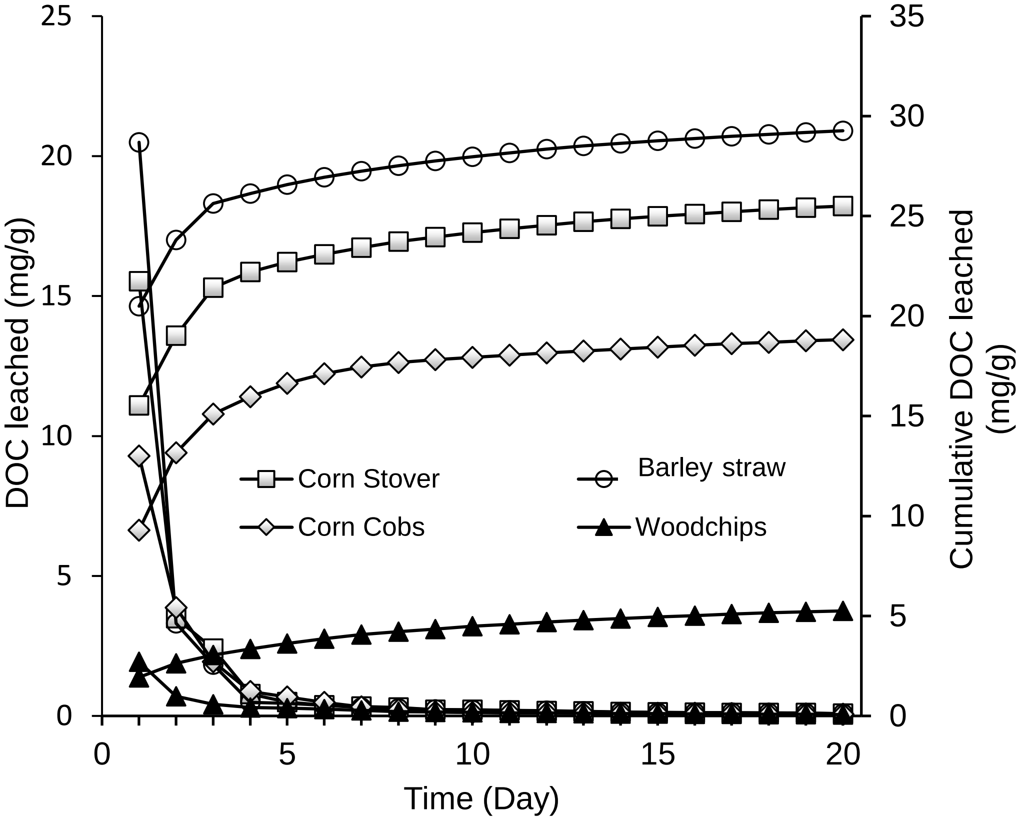


Figure 4.1. Variation of leaching DOC from different materials

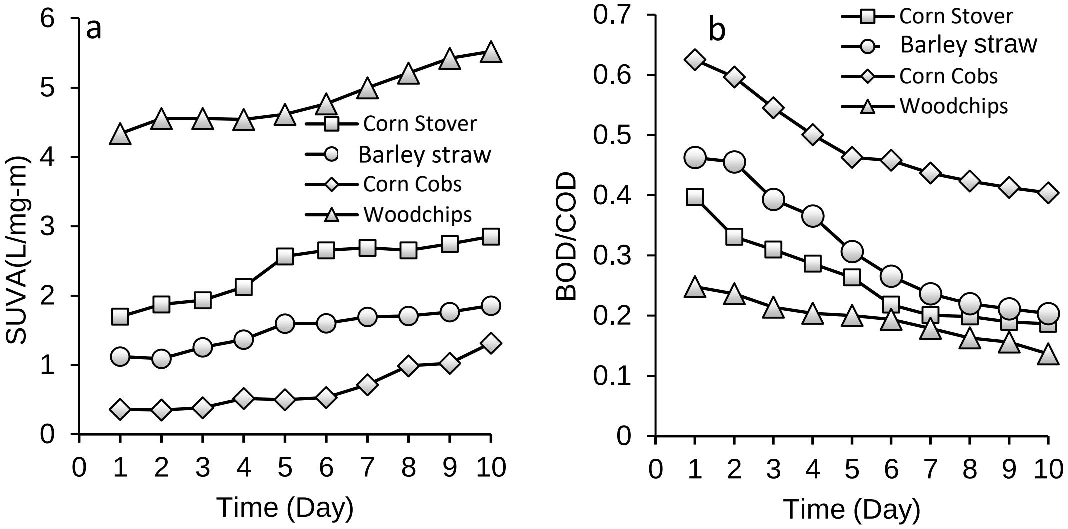


Figure 4.2. **SUVA and BOD/COD profiles during leaching test**

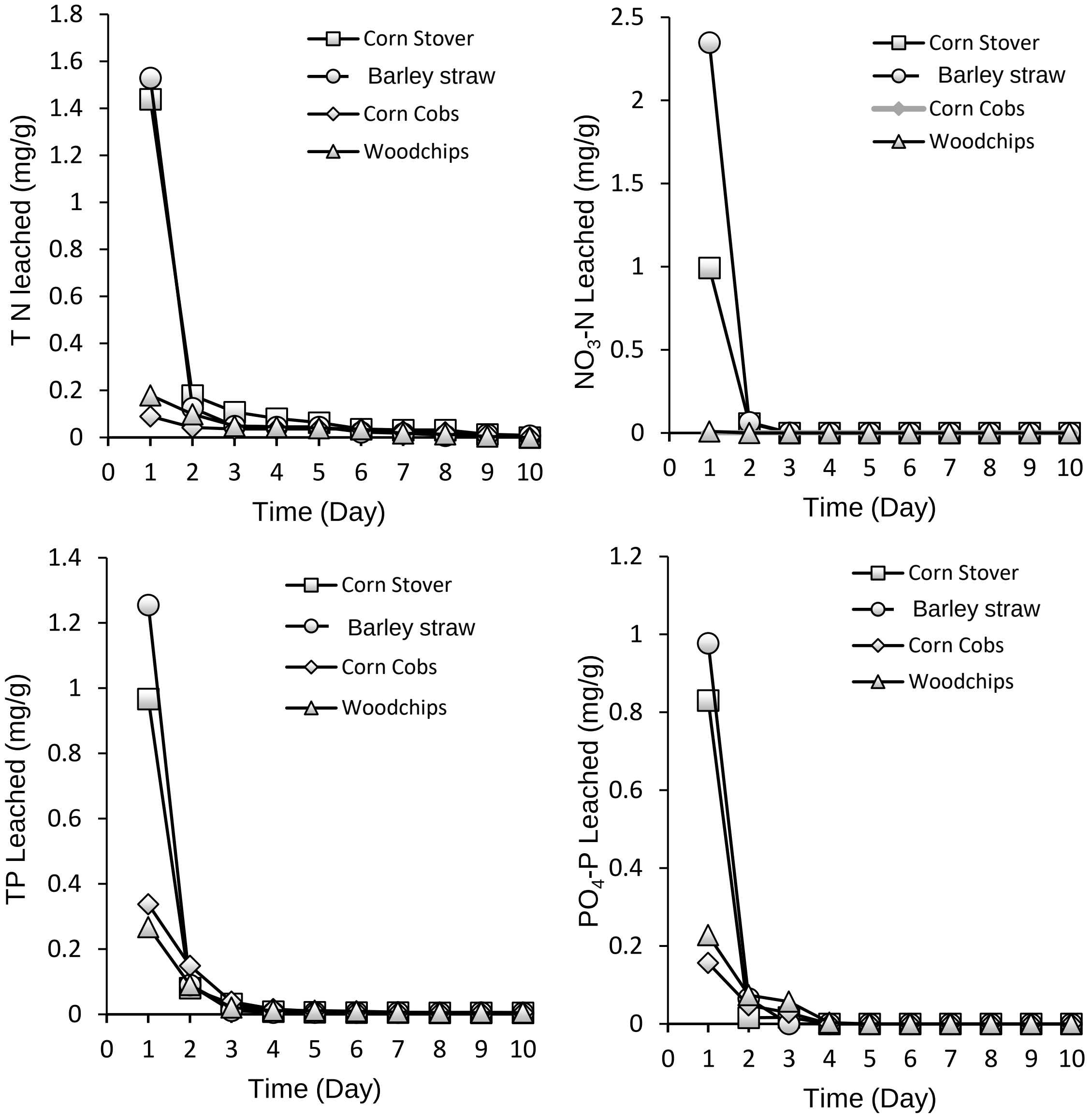


Figure 4.3. Leaching TN, NO_3^--N, TP, and PO_4^{3-}-P by different materials

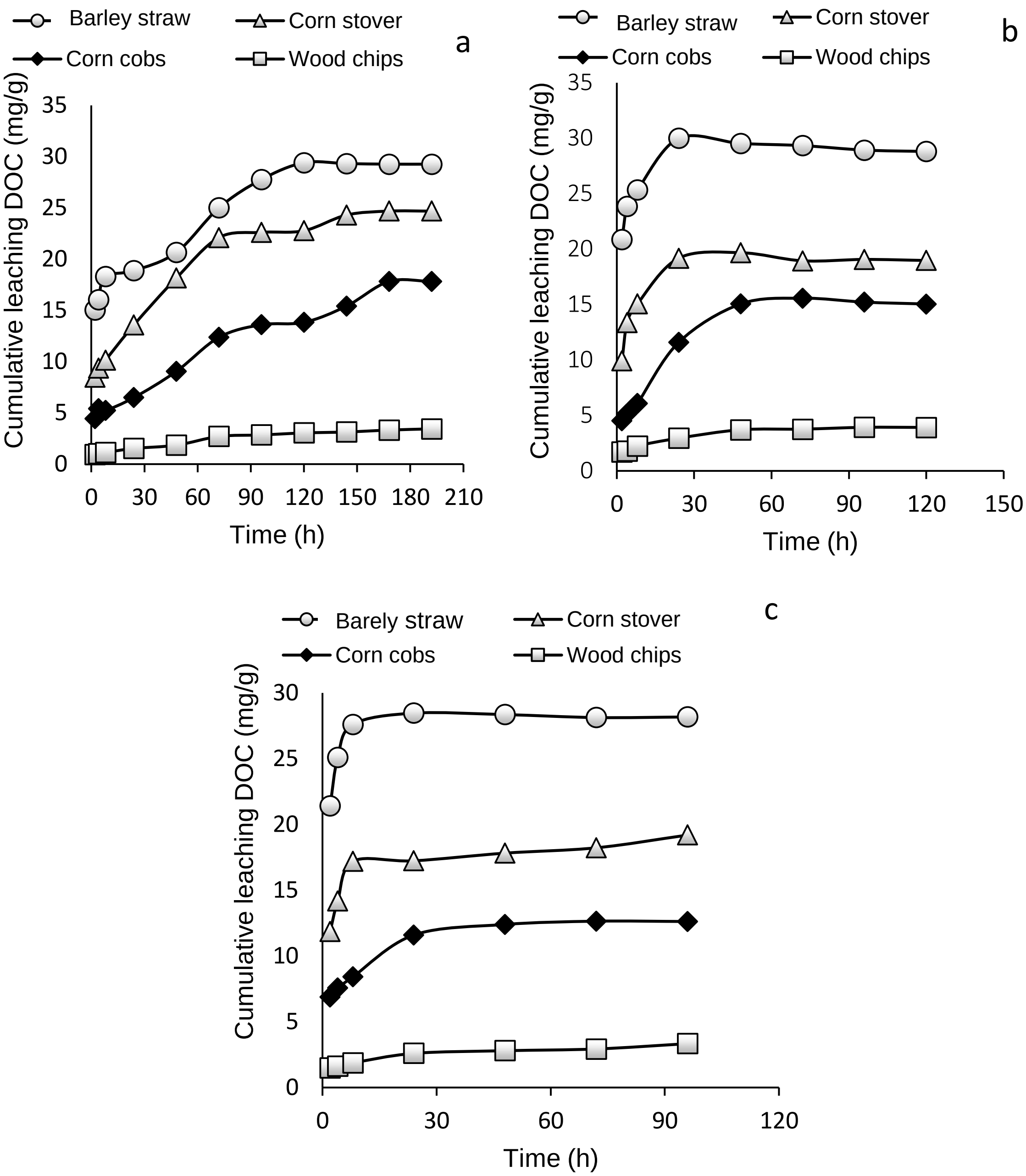


Figure 4.4. **Effect of temperature on DOC leaching; a) 10 ˚C, b) 20 ˚C, c) 30 ˚C**

Chapter 5: Overall Conclusion

Cyanobacterial blooms are generally triggered by eutrophic conditions due to anthropogenic nutrient inputs to surface waters. During the bloom, some species produce toxic (cyanotoxins) that are dangerous for humans and animals. Phosphorous (P) and Nitrogen (N) are known to be limiting factors in eutrophication condition and can enter to the aquatic ecosystem via different sources. To evaluate the use of natural minerals to enhance the precipitation of phosphorus and cyanobacteria during alum coagulation, and to reduce phosphate release during sediment capping, laboratory coagulation experiments were conducted on a lake water spiked with Anabaena sp. using alum and four natural minerals (zeolite, calcite, limestone, and sand). Long-term column sediment capping experiments were conducted using different minerals after alum coagulation to evaluate their effectiveness in reducing phosphate release. The results showed that alum coagulation was able to remove 85-90% of phosphate and chlorophyll α from Anabaena sp. enriched lake water samples. The added natural particles did not substantially affect the removal of phosphate and chlorophyll α during combined alum and particle coagulation. However, natural particles substantially increased the floc settling kinetics during coagulation. The combined treatment with alum and particles also increased the resistance of the sediment to disturbance by mixing. The long-term sediment capping experiments showed that capping with natural minerals substantially reduced the levels of phosphate released from the sediment.

Lake water spiked with Anabaena sp. was also treated with PAC, phoslock, and the combination of these two technologies to evaluate their removal efficiencies for phosphate, chlorophyll α, and dissolved organic carbon (DOC). The results showed the combination of PAC and phoslock effectively removed phosphate, chlorophyll α and DOC at lower doses than PAC or phoslock alone. The combined use of PAC and phoslock exhibited high tolerances to the variations in pH and DOC levels during coagulation. The combination of PAC and Phoslock also increased the settling kinetics of the flocs.

To enhance denitrification bioreactors performance for removing nitrate-nitrogen, easily biodegradable organic compounds are needed. Woodchips are the most commonly used organic substrate in denitrification bioreactors for subsurface treatment. However, some of the aromatic organic compounds leached from woodchips may not be easily biodegradable which can limit the denitrification efficiency. Organic carbon media derived from agricultural residues such as corn cobs, corn stover and barley straw can produce high quantities of easily biodegradable carbon to support denitrifying microorganisms in bioreactors. The DOC leaching characteristics of selected agricultural residues were evaluated in this study. The results showed that the DOC leaching potential followed the order of barley straw> corn stover > corn cobs >woodchips. Agricultural residues also exhibited faster DOC leaching kinetics and higher biodegradation potentials than woodchips. Although agricultural residues leached higher concentrations of nutrients during initial flush, those concentrations quickly declined within several days of leaching.

Overall, the results of this study suggest that natural minerals could be used as effective coagulation aids to facilitate floc settling and prevent floc resuspension during lake water coagulation. Natural minerals could also be used as effective capping materials to reduce phosphate releases from sediment after coagulation treatment. PAC and phoslock could be used simultaneously to effectively precipitate phosphate and cyanobacteria in lake waters, and organic substrates derived from agricultural residues are well suited for the application of denitrification bioreactors.

Additional research to determine the effect of alum, PAC and phoslock coagulation with the aid of minerals in cyanotoxins removal is recommended. To further understand the effect of sediment capping on microorganism existed in the interface between sediment and water future researches are suggested. Analyze the true costs associated with harmful algal bloom events and its control in order to provide a better basis for decision-making is recommended. Develop a model to monitor the algal bloom response to varying environmental conditions like nutrient loading and light is suggested.

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