Investigation of direct-reduced iron as a filter media for phosphorus removal in wastewater applications

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ABSTRACT

Passive reactive filters have the potential to provide effective phosphorus (P) removal from stormwater or agricultural drainage, or to act as an add-on P-removal technology for decentralized or small community wastewater treatment systems. Passive filters require minimal energy consumption and human maintenance. Direct-reduced iron (DRI), a steel-making intermediate, was investigated as a passive filter media for wastewaters phosphorus reduction.

Phosphorus is a biologically active element that is in excess in many natural water ways due to intensive human activity. Eutrophication can occur when P concentrations exceed 0.02 mg/L in freshwater lakes and rivers. The harmful consequence of this phenomenon includes oxygen deprivation, fish death and cyanobacteria-produced toxins. There is a pressing need to limit phosphorus over-discharge into natural waterways.

DRI is a novel media in the application of wastewater treatment and was characterized to have a porous structure with high metallic iron content. The phosphorus retaining mechanisms in batch and column studies suggest a combination of adsorption and surface crystal formation as the dominant removal mechanisms. Batch studies demonstrated increasing removal capacity with P concentration with a plateau observed at 21 mg P/g DRI relating to initial 3000 mg P/L. Media rejuvenation was investigated through chemical treatment with two iron solutions ($Fe_2(SO_4)_3$, $FeCl_3$) and two acidic solutions (H_2SO_4 and HCl) at varying molarity. P removal capacity could be fully recovered with 0.05 M Fe^{3+} or 0.4 N H^+ (HCl/H_2SO_4), while a 37.6% P recovery was also achieved in an acidic solution at 1.2 N H^+ (HCl/H_2SO_4).

A column study utilizing three media sizes of DRI (3.5, 11, 19 mm) and one media size of activated alumina (AA) (7.5 mm) was conducted for 315 days using synthetic P solution varying from 2 to 10 mg/L and hydraulic retention times (HRTs) varying from 0.7 – 15 h. The results demonstrated that removal efficiency increased with HRT and decreased with increasing media size and concentration with minimum HRTs to maintain an 80% removal efficiency varying from 4.4 to 15 hrs for DRI and 3.9 hrs for AA for influent P concentrations of 10 mg/L and below. After 1 year of column operation, the DRI media had demonstrated a minimum removal capacity of 1.82 mg P/g DRI, which can be used as a conservative design parameter. A short duration column study (34 days) utilizing municipal lagoon effluent exhibited similar removal efficiencies to the synthetic column study under the same operational conditions. The 10 years lifespan DRI filter with 80% removal rate in the treatment of stormwater, municipal lagoon effluent, septic tank effluent and dairy wastewater application would have been estimated to have filter volumes of 0.24, 4.69, 15.3 and 36.2 m^3, respectively.

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LIST OF ABBREVIATIONS

ATP	Adenosine triphosphate
BET	Brunauer-Emmett-Teller theory
BOF	Blast oxygen furnace
CAPEX	Capital investment
CCRI	Centre for Catalysis Research and Innovation
CIP	Clean-in-place
COD	Chemical oxygen demand
DRI	Direct-reduced iron
EAF	Electric arc furnace
FAO	Food and Agriculture Organization
EDS	Energy dispersive X-ray spectroscopy
HBI	Hot briquetted iron
HRT	Hydraulic retention time
ICP-OES	Inductively coupled plasma - optical emission spectrometry
LDPE	Low-density polyethylene
M.A.Sc	Masters of applied sciences
NOM	Natural organic matter
OPEX	Operating costs
rpm	Revolutions per minute
SEM	Scanning Electron Microscope
SG	Specific gravity
SOCs	Synthetic organic compounds
SRP	Soluble readily phosphorus
TN	Total nitrogen
TP	Total phosphorus
TSS	Total suspended solid
USEPA	United States Environmental Protection Agency

CHAPTER 1 : INTRODUCTION

1.1. BACKGROUND

Phosphorus is an essential element that constitutes DNA compounds and cell membranes of plants and creatures on earth. It is also involved in several biological processes, including energy production, cell signaling and so on.

Phosphorus is especially important to the agricultural industry. Adding phosphorus to soil low in available phosphorus can promote root growth and winter hardiness, hasten maturity and boost yields. Since the 1950s, the substantial usage of phosphorus as fertilizer in the agricultural industry and the increase of phosphorus imbalance caused by the intensification of livestock practice have induced an environmental concern - eutrophication. Uncontrolled algae, cyanobacteria and aquatic plant growth affect water chemistry, most importantly, reducing oxygen levels in water bodies as excess biomass decomposes, which can result in fish kills and impair aesthetic and recreational functions of the natural waters. Additionally, the eutrophic production of blue-green algae (cyanobacteria) can have a detrimental impact on public health with the increases of the mass of organic compound which can generate cancer-inducing disinfection by-products (DBPs) when in contact with chlorine.

The Canada-U.S. Great Lakes Water Quality Agreement set up the commitment in 2012 to "*Assess, develop, and implement programs to reduce phosphorus loadings from urban, rural, industrial and agricultural sources. This will include proven best management practices, along with new approaches and technologies.*" In 2016, the agreement adopted a 40% total phosphorus load reduction target to prevent further damage

to Lake Erie. Canada and the United States require less than 1 mg/L total phosphorus discharge of effluent nationally and 0.1 mg/L total phosphorus when discharge to the sensitive water body. In most European countries, water discharge cannot contain more than 1 mg/L TP. In Australia, effluent quality parameters are more stringent with 0.01 - 0.1 mg/L at South Australia, 0.3 mg/L in New South Wales and 0.5-1 mg/L in Victoria (Environment and Climate Change Canada, 2018).

The traditional and commonly applied method to reduce phosphorus in wastewater is through chemical precipitation by dosing hydrated aluminum sulfate, ferric chloride/sulfate, or lime ($Ca(OH)_2$). Chemical costs can be significant, and coagulation increases the sludge volume produced by the wastewater treatment plant. Since chemical precipitation requires a degree of continuous O&M including chemical management and access to electricity, chemical precipitation is not feasible for many decentralized applications including agricultural and urban runoff and decentralised wastewater systems. Alternatives utilising passive adsorptive media have been investigated to better address this need of increasing environmental concern.

A novel material, direct-reduced iron (DRI), was investigated as a potential media of interest for phosphorus retaining filters in this thesis. DRI has been widely used in the steel-making industry due to its fuel efficiency, but it is rarely used in the water treatment industry. DRI has high metallic iron content and a porous surface structure, which provides a good potential as a phosphorus adsorptive media.

1.2. STUDY OBJECTIVES

The objective of this study is to provide a fundamental understanding of phosphorus removal capacity of direct-reduced iron, a new media for aqueous phosphorus removal by investigating media characterization, phosphorus retaining capacities, and column study performance. This study used synthetic water in batch trials and column experiments under various conditions as well as domestic wastewater lagoon effluent to compare the P removal performance. Total and ortho-phosphorus in the experiment were analyzed and other related parameters of pH, conductivity and dissolved iron. The specific objectives of this research are as follows:

- Characterize the DRI media in terms of density, specific surface area, surface morphology and elemental composition;
- Determine phosphorus removal mechanisms and retention capacities;
- Develop methods for media rejuvenation and P recover from saturated media;
- Study the impact of design parameters (media diameter, HRT, media filling percentage) and operating conditions (influent concentration, temperature) on removal efficiency during column operation
- Estimate the lifespan of DRI filters for typical wastewater applications.

1.3. THESIS ORGANIZATION

Chapter 1 presents background information on the topic of phosphorus pollution in natural waterways, current phosphorus discharge regulations in Canada and around the world, the existing phosphorus retaining technologies and emerging media direct-reduced iron utilized in the water treatment industry. Chapter 1 also presents the significance of the research and the objectives of the study. Chapter 2 presents a literature review of the source of phosphorus, the causative reasons for phosphorus pollution and the mitigation strategies for phosphorus-induced environmental concerns. Chapter 3 describes the detailed laboratory experiments and the methodologies used to perform this study.

Chapter 4 presents the results of the DRI characterization physically and chemically. Batch tests were conducted based on P concentration and the maximum P removal capacity per unit of media was determined. Phosphorus crystals were observed on SEM photos and the retention mechanism was also discussed. Finally, chemical treatment media rejuvenation and P recovery were investigated.

Many factors that potentially affect P removal efficiency in column studies were evaluated, including media diameter, influent P concentration, water quality, HRTs, media filling percentage and temperature. They were investigated in chapter 5. The design values of HRTs and influent loading rate was given based on maintaining 80% removal rate. The removal rate was arbitrarily selected to represent a relatively high level of treatment. The life spans and volumes of DRI filters were estimated based on four types of P-untreated wastewaters with proposed minimal HRTs.

Finally, Chapter 6 presents all conclusions resulting from this study in regard to DRI as a filter media for P reduction from wastewaters.

1.4. CONTRIBUTION OF AUTHORS

The following two manuscripts, which are based directly on the results of this study. The author's contributions to the work are described below.

Article 1 (chapter 4):

H. Qin, C. Kinsley and P. M. D'Aoust.

Investigation on phosphorus removal capacity utilizing direct-reduced-iron (DRI): batch studies and media rejuvenation.

H. Qin: Designed, conducted experiments and performed laboratory analytical procedures. The writer of the thesis manuscript.

C. Kinsley: Developed the research question, provided supervision in the development of experimental procedure, analysis of results and revision of the manuscript.

P. M. D'Aoust: Provided expertise, technical and logistical support. Also aided manuscript revisions.

Article 2 (chapter 5):

H. Qin, C. Kinsley and P. M. D'Aoust.

The factors that affect direct-reduced iron (DRI) column on the phosphorus reduction efficiency.

H. Qin: Designed, conducted experiments and performed laboratory analytical procedures. The writer of the thesis manuscript.

C. Kinsley: Developed the research question, provided supervision in the development of experimental procedure, analysis of results and revision of the manuscript.

P. M. D'Aoust: Provided expertise, technical and logistical support. Transported wastewater for experimental need. Also aided in manuscript revisions.

1.5. REFERENCES

Environment and Climate Change Canada. (2018), *Canada's Challenges and Opportunities to Address Contaminants in Wastewater (Supporting Document 2)*, Environment and Climate Change Canada, Canada. [online] http://cwn-rce.ca/wp-content/uploads/projects/other-files/Canadas-Challenges-and Opportunities-to-Address-Contaminants-in-Wastewater/CWN-Report-on-Contaminants-in-WW-Supporting-Doc-2.pdf.

CHAPTER 2 : LITERATURE REVIEW

2.1. PHOSPHORUS POLLUTION: HOW IT HAPPENED

Phosphorus is an essential element in all forms of life. In cells, it plays an essential role in the adenosine triphosphate (ATP) cycle, powering cell metabolism in most uni - and pluricellular organisms. In plants, phosphorus stimulates root growth, enhances winter hardiness and accelerates maturity (Mardamootoo et al., 2010).

Unfortunately, if it is allowed to enter the natural environment, it can also accelerate the natural aging of lakes and streams by increasing the biological productivity, leading to excessive growth of macrophytes and algae which can lead to generalized hypoxia and eutrophication. Phosphorus (P) is the most critical nutrient mankind can attempt to control in fresh water, as its presence in the natural environment stimulates widespread growth of macrophytes and algae and the causes general impoverishment of surface water quality characteristics. In the natural environment, phosphorus will be a limiting nutrient due to the continuous transition and fixation of nitrogen (N) and carbon (C) between the atmosphere and water (Correll, 1998). In order to prevent the development of hypoxia and eutrophic conditions in surface water bodies, phosphorus concentrations should be kept below between 0.01 - 0.02 mg/L-P. Beyond these concentrations, the risk of eutrophication will be heightened (Hasler, 1947; Vollenweider, 1970).

Advanced eutrophication of surface waters is highly deleterious to the intrinsic value that water bodies have for local or regional economies – eutrophication-impacted waters will be less suitable for fisheries, industrial operations, as a source of drinking water or as a recreational location. Nutrient-induced algae blooms also contribute to a wide range

of problems, including fish kills (due to oxygen deprivation) by the anaerobic decomposition of aquatic weeds and heightened diurnal respiration effects (Hallegraeff, 1993), the killing of livestock by water-soluble toxins released by Blue-green algae (Beasley et al., 1989; Saker et al., 1999), and the formation of trihalomethane and other disinfection by-products during drinking water disinfection (Kotak et al., 1994; Lawton and Codd, 1991; Palmstrom et al., 1988; Tomerlin, 2008).

2.1.1. THE GROWTH OF THE PHOSPHORUS IMBALANCE

The rapid growth and intensification of animal husbandry have created soil phosphorus imbalances in many regions of the World. Pre-industrial farming, agricultural communities could be nutrient self-sufficient in that they produced enough crops to meet livestock feeding requirements, which in turn would generate the manure required to meet all crop nutrient needs. During the 1950s, the development of more intense farming systems and practices led to the rise of highly specialized grain, cereal and livestock operations, resulting in the concentration of industrial farming in certain specific regions. Coupled with fluctuating year-to-year crop prices and the concept of cash-crops, many smaller agricultural operations also switched to more specialized mono or dual-cultures (Clark and Tilman, 2017; Yahya et al., 2017), often leading to soil impoverishment and soil phosphorus saturation. In the U.S., less than one-quarter of farm-produced crops are fertilized by the manure which is produced from the livestock on site. This leads to widespread movement of nutrient-rich manure across geographical zones due to the intensification of agricultural practices. Wastewater treatment plant biosolids will also sometimes be applied to land as fertilizers, resulting in a translocation of phosphorus and nitrogen via the food imported from around the World. These agricultural transformations

and change in practices have led to the accumulation of phosphorus in the soils of intensive livestock production areas. An investigation conducted by the Food and Agriculture Organization of the United Nations (FAO) determined that the livestock and animal husbandry industries of

Thailand, Vietnam, the Guangdong province of the P.R.C. and the United States contributed to 14%, 38%, 72% and 33% of their total nitrogen and 61%, 92%, 94% and 32% of their total phosphorus loads released to the environment, respectively (FAO and LEAD, 2006).

The second major cause of phosphorus imbalance is the mismatch between the applied phosphorus as manure and the actual nutrient needs. In areas where intense animal husbandry is performed, manures are sometimes applied at rates which are designed to meet nitrogen nutrient requirements for crops, but neglect the excess addition of phosphorus. The needed N:P ratio of terrestrial plants in the natural environment varies widely, from approximately 1 to 100, however, with an average N:P ratio of 12 to 13 (Sabine, 2004). Meanwhile, the N:P ratios of pastureland under the effect of stockpiling are in the range of 0.63 to 1 for cattle manure, and approximately 4.23 for liquid pig manure (Manitoba Agriculture, 2015). OMAFRA manure fact sheet (Brown, 2013) provided other N:P ratios of livestock manure ranging from 1.19 to 6.25 depending on the type of livestock. Therefore, the P content of manure resulting from animal husbandry is in great excess compared to the natural environment of terrestrial plants.

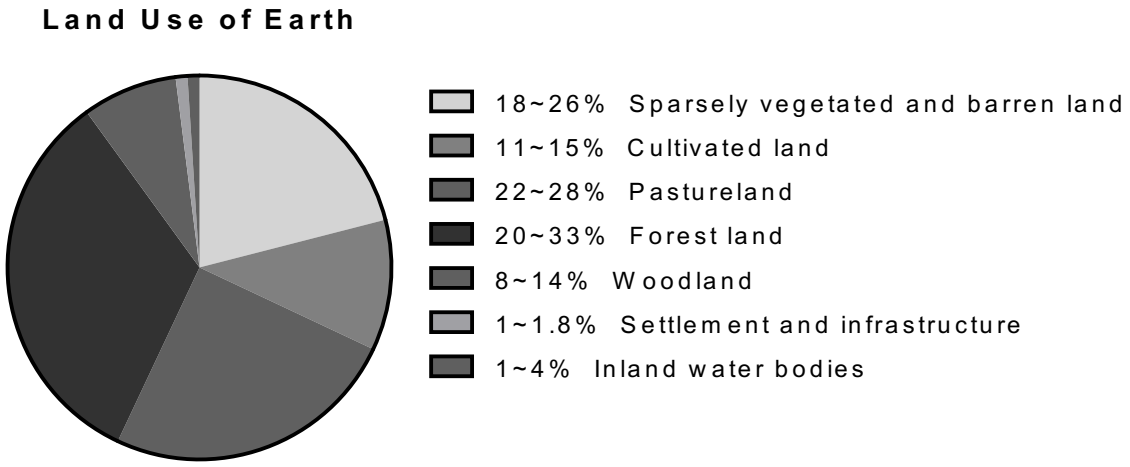

Figure 2.1. Land use percentage of Earth (adopted from FAO, 2011)

In the early 21st century (Figure 2.1), 3.29 billion ha (25%) of Earth's land area (13.2 billion ha) was utilized as pastureland, which includes usage for animals to graze, and 1.6 billion ha (12%) of global land is used for agricultural crops practice (FAO, 2011). This clearly illustrates the large land footprint of animal husbandry practices and crop industry.

2.1.2. MECHANISMS OF PHOSPHORUS TRANSPORT

The conveyance of phosphorus in runoff occurs in two forms: particulate and dissolved. Particulate phosphorus includes P associated with soil particles and organic matter eroded during high flow runoff, erosion-causing rainfall or storm events. Dissolved phosphorus is mainly ortho-phosphorus that slowly released into water through de-fixation.

In soils, phosphorus generally exists in organic (25-50%) and inorganic (50-75%) forms. Inorganic phosphorus compounds range from soluble fertilizer residues, slowly soluble calcium phosphate or very stable ferric and aluminum oxides. Organic phosphorus compounds are comprised of readily available undecomposed plant residues and microbes.

Plants typically only take up inorganic soluble phosphorus, which breaks down from organic phosphorus by mineralization and through desorption from readily available inorganic phosphorus compounds. Microbial activity controls the mineralization of organic phosphorus and physical/chemical bonds govern the desorption and fixation of inorganic phosphorus (Brookes et al., 1982). Phosphorus tends to accumulate in the surface soil at a depth of 50 to 125 mm from the surface. Additionally, because of phosphorus recycling from plant roots to soil above the roots, phosphorus can be redeposited in the crop residues on the soil surface where biological activity is most stimulated.

Runoff and soil erosion have been identified as the main mechanism by which phosphorus and sediment are exported throughout watersheds. Agricultural runoff percolates through the soil and brings sediments downstream. It has been observed that up to 90% of the phosphorus transported from farmland is attached to soil particles and sediment (Sharpley, 2001), which provided a long term soluble phosphorus source in the downstream watershed.

2.2. PHOSPHORUS AND MODERN AGRI-FOOD PRACTICES

2.2.1. PHOSPHORUS IN AGRICULTURAL FERTILIZER

The intensive use of inorganic phosphorus did not occur until the 1950s, where it began being extracted industrially from phosphorus containing minerals/ore, called “phosphorus rock”. Currently, the usage of inorganic phosphorus fertilizer chemicals such as monocalcium phosphate and monopotassium phosphate is widespread, with both of the

compounds extracted from phosphorus rock. Since the 1950s, nearly half a billion tonnes of phosphorus have been extracted via phosphorus mining (Cordell et al., 2011). Phosphate rock is a non-renewable resource, and global reserves are estimated to last for only another 50 to 100 years (Cordell et al., 2009).

Substantial amount of P fertilizer has been applied to crops, causing P over-fertilization (P > 100 mg/kg) in several countries and regions. For example, over half of the land utilized for crop growth in Mauritius currently experiences phosphorus exceedance (Mardamootoo et al., 2010) and in Germany, total P content in soil is up to two times higher than unfertilized soils, and available P contents are up to six times higher in agricultural lands than in unfertilized soils (Medinski et al., 2018). Global warming has also introduced more extreme weather patterns in most of North America and some regions of Europe, causing more frequent, stronger precipitations and winds, which will continue to aggravate soil erosion. These factors have made it easier to observed vast phosphorus migration of P into the hydrosphere, greatly changing the natural global phosphorus cycle and contributing to an uptick in global eutrophication (Cordell et al., 2011).

The USEPA has determined that agricultural and intensive livestock husbandry practices are the main causes for the contamination of phosphorus sensitive streams and lakes such as Lake Erie (Daniel et al., 1998). With 50% of lakes and 60% of rivers affected by nutrient input, eutrophication is becoming the critical problem impairing water quality in Canada and the United States (Cole and Weihe, 2015; Parry, 1998; USEPA, 1996).

Eutrophication is a difficult problem to solve due to the fact that the deleterious effects caused by excessive nutrients entering natural waters is sometimes only observed

remotely, far from the original point of pollution/discharge. Furthermore, phosphorus pollution will often be entering the environment via non-point source pollution, blurring the exact source. By the time the water quality effects are noticeable, it has already become difficult and expensive to implement remedial strategies. This is sometimes further complicated by the fact that surface waters often cross political boundaries, leading to situations with different governments having very different interests (Sharpley, 2001).

Phosphorus retaining strategies should be therefore adopted to reduce the impact of human-induced agricultural practice. Failure to address phosphorus pollution problems could lead to severe environmental issues which will likely have disastrous effects on the natural environment, our way of life and humankind as a whole.

2.2.2. ANIMAL HUSBANDRY AND THE DAIRY INDUSTRY

Much of the additional phosphorus entering the environment is doing so via agriculture, due to changing and more intensive farming practices (Heathwaite and Johnes, 1996; Johnes and Burt, 1993; Roberts and Marsh, 1987). The increased use of nutrients in crops destined to livestock feed has also been observed to cause an increase in livestock nutrient pollution via their excreta (Baxter et al., 2003). In most cases, the N:P uptake ratio of plants is bigger than manure's N/P ratio. Due to P over-supplementation in livestock's diet, it was identified that the N:P ratio was approximately 2.6 for feedlot manure and 1.9 for composted manure (Eghball et al., 1997). However, the ideal nutrient ratio for plant uptake ratio ranges from 4.5:1 to 9:1. The imbalance between the N:P ratio in manure leads to excessive P in the soil of application rates of manure are based on N requirement (Eghball and Power, 1999).

The dairy industry often produces cyclical but non-constant wastewater effluent. Universal quantification of all dairy waste is difficult due to significant variance in effluent characteristics, based mostly on the number of animals, the type of dairy operation and the clean-in-place (CIP) procedures implemented on-site at the time of production (Danalewich et al., 1998; Rivas et al., 2010). The use of CIP products such as (ortho)phosphoric acid can significantly impact phosphorus loading of dairy effluent. Regardless of CIP procedure, phosphorus concentrations in dairy effluent remain relatively high. An investigation of fifteen dairy plants performed in 1998 revealed mean effluent flow rates range from 170 m^3/d to 1211 m^3/d, with an average total phosphorus concentration ranging from 37 ± 16 to 78 ± 20 mg/L-P (Danalewich et al., 1998).

Phosphorus should be controlled and managed for recovery use to address environmental issues and the emerging global challenge of phosphorus scarcity. Failure to address phosphorus recovery could lead to impacts on global food security in many parts of the world in the coming decades.

2.3. PHOSPHORUS AND STORMWATER MANAGEMENT SYSTEMS

2.3.1. THE SOURCE OF PHOSPHORUS IN URBAN STORMWATER

In the context of stormwater management systems, phosphorus is universally recognized as a deleterious substance which is undesirable. The sources of phosphorus in stormwater management systems include plant and tree litter, soil particles, pet excrement,

and fertilizers. Lawns and roads contribute to the greatest proportion of the P loading. The investigation of (Waschbusch et al., 1999) illustrated that lawns and roads could make up to about 80% of the total and dissolved phosphorus loading. Land-use was also observed to have effects on the P loading of stormwater systems. Lawns and leaf litter were found to represent a larger proportion of the P loading in residential areas, whilst roads tended to be the main cause for P loading in commercial and industrial areas (Hopke et al., 1980; Tipping et al., 2014).

Dissolved phosphorus accounts for approximately 45% of the total phosphorus present, but the phosphorus fractionation ultimately depends on land use within the watershed. For example, dissolved phosphorus represents approximately 25% of the total phosphorus in road-dominated, heavily urbanized watersheds, whilst in residential areas, fallen leaves and lawns to contribute up to 50% of the P loading (Waschbusch et al., 1999).

2.3.2. RUNOFF QUANTITY AND QUALITY DUE TO URBANIZATION

Urbanization and industrialization have proceeded rapidly across the world. Today, the most urbanized regions include Northern America (82% by area), Latin America and the Caribbean (80% by area) and Europe (73% by area) (Bocquier, 2005; Seto et al., 2010). Urbanization increases the quantity and proportion of impervious areas such as roads, parking lots, roofs and sidewalks within a watershed, which reduces infiltration and evapotranspiration (Burton and Pitt, 2001). This, in turn, causes an increase in runoff quantity, leading to more frequent and higher peak flows. (WEF, 2012; Zahmatkesh et al., 2015) For example, a 1-year storm peak flow increased from 0.6 m^3/s to 1.6 m^3/s over a

10-ha watershed after being converted from pastureland to a residential area with 35% imperviousness in Columbia, Missouri. (WEF, 2012)

Urban stormwater characteristics are usually heterogeneous and are heavily influenced by the use of the receiving watershed, leading to a high degree of geographic variability (Vincent and Kirkwood, 2014). Stormwater runoff tends to transport non-point sources pollutants such as total suspended solids, total nitrogen, total phosphorus, biological oxygen demand, heavy metals, hydrocarbons, pathogens, trash and debris, which could require treatment before release to receiving waters.

Concentrations of total phosphorus in urban stormwater runoff are highly variable and dependent on land use and degree of urbanization. However, the median observed concentrations are generally similar over different land uses. Table 2.1 below outlines the median, minimum and maximum observed total phosphorus concentrations in different types of stormwater runoff.

Table 2.1. Median, minimum and maximum observed total phosphorus concentrations in urban stormwater runoff (adapted from International Stormwater BMP Database, 2004)

Land use	***Median (mg/L)***	***Minimum (mg/L)***	***Maximum (mg/L)***
Commercial	0.2	< 0.01	4.27
Industrial	0.23	< 0.02	7.9
Residential	0.26	< 0.01	19.9
Open space	0.13	< 0.01	0.76
Native prairie	0.3	0.01	0.5

Since observed stormwater quantities vary significantly, the total phosphorus quantity exported from a specific watershed may differ importantly, even when similar *in-situ* concentrations are observed. To account for this, total phosphorus transport is generally expressed as a function of mass per land area per unit of time (for ex.: $g/m^2/yr$). Typical annual total phosphorus land mobilization rates are shown below in Table 2.2.

Table 2.2. Typical total phosphorus transport rate from various different land-use cases (adapted from (Jeje, 2016; Liu et al., 2012)

Land use	*Range ($g/m^2/yr$)*	*Recommended ($g/m^2/yr$)*
Native grass	0.00 – 0.04	0.01
Forest	0.00 – 0.03	0.01
Pasture	0.03 – 0.10	0.08
Corn/soybean	0.20 – 0.38	0.25
Mixed agriculture	0.05 – 0.11	0.08
Low density residential	n/a	0.12
High density residential	n/a	0.15
Commercial	n/a	0.22
Highways	n/a	0.35

2.3.3. FATE OF PHOSPHORUS IN STORMWATER SYSTEMS

The purpose of stormwater control has been to mitigate flooding, protect life, limit damage to property and reduce the number of pollutants and other deleterious substances entering the receiving waters via stormwater management structures such as basins, swales and strips, filters, infiltrators and gross pollutant traps. (WEF, 2012). Stormwater management structures have proven positive effects on flood mitigation and are now becoming an integral part of municipal planning across the world (Jiang et al., 2018; Marsalek et al., 2005; Porse, 2013).

Stormwater management systems are typically effective at reducing suspended solids and pathogens, and are capable, depending on the configuration of the systems, to reduce biological oxygen demand, metals and total nitrogen to some extent. Due to the high content of phosphorus existing in organic form, around 43% of the P loading will be retained in stormwater systems via solids removal with little readily soluble phosphorus (SRP) removal (Lake Simcoe Region Conservation Authority, 2013). However, phosphorus may be re-released at a later date as water-soluble orthophosphates in stormwater systems due to strong microbiological activities. Also because of the sufficient iron ion in the freshwater and benthic sediment, iron phosphate is a common form in the stormwater pond (Olsen, 2017; D'Aoust et al., 2017). The hydrogen sulfide generated through sulfate-reduction reaction under reducing conditions can break the iron phosphate chemical bonds and release phosphorus back to the water (D'Aoust et al., 2017; Song et al., 2017).

2.4. PHOSPHORUS AND DOMESTIC WASTEWATER

2.4.1. CENTRALIZED DOMESTIC WASTEWATER

The percentage of the Canadian population on municipal sewers which receives secondary treatment or better for their wastewater treatment has increased from 40% in 1983 to 69% in 2009 (Environment and Climate Change Canada, 2017). The continued well-functioning of more than 3,500 municipal sewer wastewater treatment systems has been critical to the health and safety of Canadians and the natural surrounding environment (Droste and Gehr, 2018; Environment and Climate Change Canada, 2017). In the context of total phosphorus, discharge limits normally range from 0.1 to 1.0 mg/L (Environment Canada, 1992). Without P removal, TP in domestic wastewater effluent typically ranges from 3-9 mg/L (Youcai, 2016). In practice, an 80-90% removal rate is achieved at conventional wastewater treatment plants. Treatment systems will invariably have biosolids production, and depending on the municipality, biosolids will generally either be land applied as fertilizer or be landfilled (Epstein, 2010; Ødegaard et al., 2002; Sánchez-Monedero et al., 2004). There is a growing demand for P removal technologies for small community wastewater systems as P effluent limits become more stringent.

2.4.1 DECENTRALIZED DOMESTIC WASTEWATER SYSTEMS

In locations with underdeveloped infrastructure, or where larger centralized systems don't make economic sense, decentralized wastewater systems are often implemented as a viable alternative. In Canada, approximately 15% of population rely on onsite wastewater systems (Environment and Climate Change Canada, 2018), while the proportion is approximately 25% in the U.S. (USEPA, 1997). Conventional septic systems

are amongst the most commonly implemented decentralized treatment technologies, which largely reduced total suspended solid (TSS) and organic matter (BOD), with any phosphorus removal occurring through adsorption to cations in the receiving soils. Septic tank effluent typically has total phosphorus concentrations in the range of 12 - 16 mg/L-P (Crites and Technobanoglous, 1998). Therefore, there is a clear need for add-on technology for phosphorus removal for decentralized wastewater treatment applications, particularly in regions close to sensitive water bodies.

2.5. PHOSPHORUS MITIGATION AND CAPTURE OPTIONS

2.5.1. CONTROL MEASURES

Efforts in managing phosphorus to reduce the negative environmental impact should first and foremost be focused on areas having sources of phosphorus and high transport potentials (i.e. leaching, runoff or erosion). Strategies for source and transport control are listed below for different applications:

2.5.1.1. Agri-food industry:

Control measures for effluents from the agri-food industry will mainly focus on reducing the phosphorus entering sensitive watersheds.

- **Nutrient management**: Amended GLWQA agreement (2016) set up new phosphorus reduction targets with 40% P loadings reduction entering Lake Erie (Government of Canada). The commercial/industrial operations can also decrease phosphorus entering the watersheds, such as timing of application. The study

(Chaubey et al., 2010) showed that manure application in spring and summer decreased TP loss of 13.9% and 14.6%, respectively compared to late fall application, where the soil is bare and exposed to erosion and nutrient losses during spring snow melt. Ryden et al., (1974) estimated runoff loss from frozen manured land to contribute 60% (2.1 to 2.5 kg/ha) of the phosphorus in Lake Mendota. A 6% (15.6 kg/ha) losses of phosphorus happened in one winter storm event, reported by Hensler et al., (1970).

- **Buffer strips:** Buffer strips are maintained drainage areas with grass, shrubs and trees that help slow down runoff when entering the local surface waters. The vegetation contributes to trapping sediment, filtering nutrients and pesticides. They are usually built in area where runoff flows through to a waterway. The study conducted by Abu-Zreig et al., (2012) showed that the vegetated filter strips achieved 31% P removal with 2-m filter and 89% P removal in a 15-m filter with a 2.37 mg P/L concentration runoff. In general, the buffer strip has a minimum width of 3 m.

- **Soil erosion control:** Organic phosphorus is highly bound and exists in the top layer of soil. Soil erosion and soil loss directly introduces phosphorus into streams, lakes and rivers. To prevent water or wind from transporting large amounts of soil from arable land, especially sloping fields, plant cover can help to prevent phosphorus mobilization. Wind erosion can be reduced by planting shelterbelts in the dominant wind direction. Other soil erosion control practices can include the modification of agricultural practices, such as minimization of tillage, to help minimize phosphorus transport. It was reported that total phosphorus losses in

eroded soil in no till practice is 11.5% (2.4 lb/ac) of the TP loss using traditional moldboard plowing (20.9 lb/ac) (adopted from Czapar et al., calculated from 1983 data).

- **Ponds and wetlands:** Ponds and wetlands have a proven track record in reducing the total nitrogen and total phosphorus loading from agricultural practices. It is, however, essential for them to be well maintained and serviced when necessary to maintain treatment efficiency. A 2-year constructed wetlands showed the overall retention efficiency is 23% of total phosphorus (Reinhardt et al., 2005).

- **Composting of manures and sludges:** The composting of manures and sludges is considered an effective method to reduce phosphorus transport. Composting reduces the volume and the transportation costs, and concentrates the phosphorus present in the manure (Wen et al., 1997).

- **Addition of enzymes in feed to improve breakdown uptake:** Enzyme addition for livestock feed which has a significant amount of undigestible phytate (a phosphorus containing compound found in grain). Specific enzymes such as phytase can boost the efficiency of animal phosphorus uptake and potentially decrease the need for phosphorus supplements and decrease P in manure (O'Connell et al., 2005).

2.5.1.2. Stormwater management systems:

- **Dry ponds:** A dry pond is designed to hold water for 48-72 hours to settle out sediments and pollutants. It controls the peak flows of runoff, limits erosion and

also improves water quality. Between rain events, a dry pond is generally perceived as a large and low-lying area with vegetation. When it rains, the pond fills with water. Dry ponds are more common and less expensive to install than wet ponds. The EPA estimated for dry stormwater detention ponds, 19% of TP and 31% of TN could be removed (Jiang et al., 2015).

- **Wet ponds:** A wet pond is with a pond which maintains permanent standing water throughout the year. It allows sediment to settle, and incorporates some biological treatment, which removes nutrient concentrations, up to a certain extent. Wet ponds generally remove more pollutants than dry ponds due to longer water retention times. A study researched by Mallin et al., (2017) showed the TP removal rate of three wet detention ponds for stormwater runoff, with 23%, 57% and -35% TP removed respectively.

- **Construction of wetlands to treat stormwater runoff:** The surface constructed wetlands have proven track records in reducing the total nitrogen and total phosphorus loading from stormwater systems (Borne et al., 2015; Carleton et al., 2001; Perniel et al., 1998). Special attention should be given to regular maintenance of plants, especially in northern climates, where the plants may die during winter, and re-release nutrients to the aqueous environment. It is essential for them to be well maintained and serviced when necessary to maintain treatment efficiency.

- **Maintenance of stormwater management infrastructure:** Regular dredging of the forebays of wet ponds (Erickson et al., 2007; USEPA, 2004), along with water

quality characteristics monitoring will help ensure that any operation problems are detected in a timely manner, to prevent phosphorus discharge to receiving waters.

2.5.1.3. Municipal wastewater treatment systems:

- **Phosphorus concentration limitation in household cleaning detergent:** Canada lowered the phosphorus permitted in laundry detergent from 2.2% by weight to < 0.5% and introduced a limit of < 0.5% phosphorus in dishwater detergents in 2010 under the *Concentration of Phosphorus in Certain Cleaning Products Regulations* (Environment and Climate Change Canada). All commercial and industrial laundry detergents must contain less than 2.2 per cent phosphorus. The restriction of phosphorus addition in cleaning detergent contributes to 9 – 34% phosphorus reduction in household sewage. However, the phosphorus effluent before and after the phosphorus restriction showed similar trends, due to low incentive for wastewater treatment plants to pass through the reductions, instead, reductions provides a cost saving for many of the wastewater treatment plants. In Minnesota, every one percent of P decease leads to the decrease of 0.41 to 0.76 percent of phosphorus in the effluent (Cohen and Keiser, 2015).
- **Dosing of coagulants to sequester phosphorus:** By far the most popular option, a majority of North-American communities are removing or at least polishing municipal wastewater with the addition of coagulants to remove the bulk of the P loading (Narasiah et al., 1991). This method is proven, effective, and is very common. The commonly used coagulants are alum and ferric chloride and can easily reach over 80 to 90% TP removal from sewages (Ebeling et al., 2003; Youcai, 2016).

- **Construction of wetlands to polish wastewater:** Smaller communities and municipalities experiencing lower flows have had success in utilizing wetlands to polish wastewater for phosphorus removal. Subsurface horizontal wetlands and vertical wetlands have proven track records in reducing the total nitrogen and total phosphorus loading of the effluent (Chung et al., 2008). The study of Cameron et al., 2003 presented that the municipal free surface wetland achieved TP 90% and o-PO_4 82% removal for six months with average influent concentration 0.33 mg P/L.

2.5.2. CHEMICALY ACTIVE PASSIVE FILTERS

For low flow applications, particularly in less densely urbanized areas where land is not at a premium, filter-type treatment systems can be very attractive options. The size requirement for the filters will largely be dictated by the hydraulic loading and concentration of phosphorus in order to maintain an adequate contact time to reach the required treatment level.

2.5.3. STORMWATER REMEDIATION VIA IRON-BASED FILTERS

Several technologies have already been investigated to reduce the quantity of phosphorus entering receiving waters in stormwater applications. Iron-based filter media has been of particular interest and has been extensively studied (Hegemier et al., 1993; Reddy et al., 2014; Rentz et al., 2009). Engineered filters designed to capture and retain phosphorus from stormwater runoff to minimize deleterious environmental impacts have

also been studied. A less common material for phosphorus removal called slag, has also been investigated in some studies (Okochi and McMartin, 2011; Penn et al., 2012).

The investigation by Penn et al., (2012) illustrated that 21% of the P loading was removed by a filter structure consisting of steel slag with an average retention time of 18.9 mins. Okochi & McMartin, (2011) proved that electric arc furnace (EAF) slag was a compelling filter material for P removal from diverse stormwater sources. The removal efficiency achieved 1.18 mg P/g in metal-free stormwater. There is, however, research pointing to the fact that there might be competitive adsorption issues with slag filters in stormwater when other metals, especially copper, are present in significant concentrations in the urban runoff (Okochi and McMartin, 2011).

2.5.4. SLAG FILTERS

The use of slag filters began taking hold during the 1970s, in response to phosphorus removal requirement in some parts of the World, and the desire to utilize and revalorize the waste from steel production (Mercado-Borrayo et al., 2018).

Steel slag is a by-product material from steel mills. Calcium-rich slags are the most common slags and therefore, due to their abundance, many studies have utilized them to identify their suitability to be utilized for phosphorus removal. Fe-rich slag also exists and has been successfully utilized in full-scale applications. Slag filters provide a promising treatment system as post-treatments units for a passive system such as wetland and facultative lagoons and as a polishing system for conventional wastewater treatment systems (Barca et al., 2014; Zuo et al., 2015).

Calcium-rich slag phosphorus removal mechanisms were studied and the general routes for phosphorus removal is via precipitation and crystallization (Drizo et al., 2006). The precipitation of phosphate occurs mainly as hydroxyapatite ($Ca_5(PO_4)_3OH$). Crystal formation takes place by filtration, settling and growth densification. The main removal mechanism is reported as precipitation since the use of slag generally leads to elevated pH conditions, due to the dissolution of calcium. Phosphorus removal declines as the calcium is depleted.

The application of slag filters comes with some significant drawbacks. High pH effluents will generally require further neutralization such as passing the effluent through a peat filter, which increases the risk of clogging, or gaseous CO_2 addition, which incurs additional operational costs. The lifespan of the material is also under debate, as many studies claim multi-year lifespans (Shilton et al., 2006), whilst some pilot applications demonstrated a lifespan as short as six months (Al Timimi, 2015). Ultimately, the lifespan very likely depends on the chemical make-up of the slag material, and so depending on ore extraction techniques and sourcing of the material, the performance and lifespan of the filters may be highly variable. Further research is likely required to identify parameters controlling better filter characteristics. The demand for frequent filter media maintenance and renewal may decrease the practicability of slag filters.

A study utilized EAF slag and basic oxygen furnace steel slag as filter media combined with a sand filter, which were treated with synthetic solution of 10 mg P/L with a 24 h hydraulic retention time (HRT) (Barca et al., 2014). Both filters reached over 98% removal over a period of 52 weeks. In the work of Mortula et al., (2007) slag achieved a promising treatment efficiency of 50% with municipal influent total phosphorus

concentrations of 3.7 mg/L. The slag demonstrated promising removal efficiencies at 99.4%, 54.1% and 59.2% with influent phosphorus concentration 0.9 ± 0.3, 0.03 ± 0.01 and 0.05 ± 0.03 mg/L, respectively (Cameron et al., 2003). Weber et al., (2007) used an EAF slag filter to treat dairy wastewater, achieving an average P removal efficiency of 75% with dissolved reactive phosphorus influent concentrations of 29 mg/L with a HRT of between 12h to 24h over a time-period of 259 days. The decline of P retaining efficiency in both periods was observed over time, with a 12% decrease at a 12h HRT and a 63% decrease with at a 24h HRT. This clearly indicates that slag filters lose efficiency over time, and with few regeneration studies available, may indicate that the filter media is not reusable and has a set lifespan.

2.5.5. NATURAL MINERALS: ZEOLITE, LIMESTONE, CALCITE AND DOLOMITE

Zeolites are aluminium-silicates which exist naturally and can also be produced synthetically. Zeolite has a porous structure and consists of silicon, aluminium and oxygen ions. Limestone, calcite, and dolomite are sedimentary rocks that are chemically stable, and which possess small cavities and a relatively large specific surface area. Limestone and calcite are largely composed of calcium carbonate, whilst dolomite contains magnesium ($CaMg(CO_3)_2$).

The mechanism of phosphorus removal by those minerals is dominated by physical adsorption, which can be described by the Langmuir model. The adsorption capacities of minerals appear to be 0.1 mg/g, 0.45 mg/g and 0.6 mg/g for zeolite, calcite and limestone respectively (Bjorn M. Sellner et al. 2019).

An alternative phosphorus retaining process receiving municipal water source by utilizing industrial by-products with high silica and calcium contents as a passive filter system. This has been studied in conjunction with a constructed wetland (Barca et al., 2014; Cameron et al., 2003; Hylander et al., 2006; Mortula et al., 2007). Such products include slags, shell sands, opoka and Polonite®.

In one study, Polonite® achieved significant P retaining capacity as 1.3 mg P/g while slags, opoka and sands performance below 0.5 mg P / g in a study performed by Hylander et al. (2006). Detailed information of common phosphorus retaining adsorbents are summarized in Table 2.3.

Table 2.3. Common phosphorus retaining adsorbents in literature

Material	Diameter (mm)	Composition	P sorption capacity (g P/kg)	Experimental conditions	Reference
BOF	9.5-19	42%CaO, 6%MgO, 0.3%Fe_2O_3, 15%Al_2 O_3 0.2%CaO,	0.42 (batch)	40 ml of varying phosphorus concentrations (5 – 100 mg P/L) with 20 g substratum under shaking condition	(Mann and Bavor, 1993)
EAF	2.5-10	21.7% Ca, 7.9% MgO, 24.3% Fe_2O_3, 2.5% Al_2O_3 , 6.4% Si	3.93 (batch, column)	700 ml of P solution (1 – 320 mg/L) with 35 g media under shaking condition	(Drizo et al., 2002)
Zeolite	6-13	Aluminum-silicate	0.46 (batch)	2.5 – 40 mg P/L initial concentrations, were equilibrated with 20 g of the substrate under shaking condition	Adapted from (Drizo et al., 1999)

Limestone	0.25-2	53% $CaCO_3$, 4% MgO	0.6	2.5 – 40 mg P/L initial concentrations, were equilibrated with 20 g of the substrate under shaking condition	(Drizo et al., 1999; Johansson, 1999)
	6-14		0.25	5 – 25 mg P/L 50 ml solution with 1 g media, under shaking condition	
Dolomite	2-5	$CaMg(CO_3)_2$	0.15 (batch)	10 g media with 50 ml P solution (2.5 – 100 mg/L) under shaking condition	(Prochaska and Zouboulis, 2006)
Calcite	2-6	$CaCO_3$	0.015 (batch)	1 g media was shaken with 1 – 100 µM P/L solution of 20 ml	(Sø et al., 2011)
Polonite®	2-5.6	Natural calcium silicate	>1.3 (Column)	5 mg P/L solution was pumped to the top of the 90% media column three times a day for 68 wk	(Renman and Renman, 2010)
Shell sands	3-7	32.8%Ca, 1.4%Mg, 0.05%Fe, 0.03%Al	9.5 (batch); over 90% removal rate with 1 ppm P effluent (column)	3 g of media were shaken in 90 ml solution with concentration 0 – 480 mg P/L	(Ádám et al., 2007)
Opoka	0.125-2	50%$CaCO_3$, 4%MgO, 5%Fe_2O_3, 10.6%Al_2 O_3, 36.2%SiO_2	0.45	5 – 25 mg P/L 50 ml solution with 1 g media, under shaking condition	(Johansson, 1999)

2.5.6. CHEMICAL PRECIPITATION VIA ADDITION OF COAGULANTS

Chemical precipitation for phosphorus removal in wastewater treatment was initially developed in Switzerland and became extensively utilized worldwide during the 1950s (Oottatep et al., 2015), in response to the spreading problem of eutrophication. It is a relatively cheap and simple treatment method to implement, and for these reasons alone remains the most commonly applied phosphorus removal technologies globally. Typical chemical precipitation involves the addition of iron (II), iron (III) and aluminium via the addition of metal salts. Lime may also be used to precipitate calcium phosphate, but it is utilized very occasionally. Physical sedimentation of phosphorus-metal precipitates will then remove phosphorus from the system.

The mechanism by which phosphorus is chemically removed in contact with ferric iron is the following: when metal salts are added to water, they will react with the water molecules and form hydrated ferric cations (Fe^{3+}). If water has an adequate amount of phosphate, a reaction between Fe^{3+} and phosphate will occur, producing iron phosphate (Thistleton et al., 2002).

Otherwise the hydrolysis products will keep reacting with surrounding water molecules and generate metal hydroxides, which are reported to be capable to adsorb phosphorus but less efficiently.

The chemical reaction between Fe^{3+} and phosphate in water is shown below:

$$Fe^{3+} + H_3PO_4 \rightarrow FeH_nPO_4^{n+} + (3-n)H^+$$
(Galal-Gorchev and Stumm, 1963) Equation 2-1

Furthermore, the presence of OH^- will promote the formation of metal hydroxides. For example, research shows that required molar ratio of Fe:P for the co-existance of iron (III) chloride and iron (III) hydroxide is 1.86 while for iron (III) hydroxide only, the molar ratio could be as high as 4.80 (Thistleton et al., 2002). Therefore, the prevention of the pre-hydrolysed metal iron is critical for the wastewater plant's operation and capital budget.

The chemical reaction between Al^{3+} and phosphate in water is same as that of Fe^{3+} and phosphate, which is shown below:

$$Al^{3+} + H_3PO_4 \rightarrow FeH_nPO_4^{n+} + (3-n)H^+$$ Equation 2-2

It has been reported that metal and P ratio is a key parameter of phosphorus removal efficiency. The higher the metal to phosphorus ratio, the higher the removal rate will be. However, in order to improve phosphorus elimination efficiency, an optimal chemical addition to phosphorus ratio is necessary for environmental and economical sustainability. Many experiments have illustrated the tendency of a stoichiometric excess of $FePO_4$ for Fe when it is reacting with P (Nesbitt, J. B., 1969; Narasiah, K. S et al., 1991). An Fe : P molar ratio of 1.48:1 (Thistleton et al., 2002) achieved 80% of total phosphorus removal with the condition that no pre-hydrolysed iron was generated. The precipitation reaction of Fe (III) with orthophosphate in water is instantaneous and forms $Fe(PO_4)\cdot 2H_2O$, known as strengite. During these experiments, mixing or agitation appeared to have little effect on the phosphorus removal performance but the initial mixing conditions are important to prevent excess chemical use and to optimize and limit sludge production due to the rapid hydrolysis

reaction of iron (III). Aluminum has a similar optimal ratio to phosphorus at around 1.5 : 1. This is expected as Al ion has the same valence state as Fe ion. High Al : P ratio leads to high P removal rates (Thistleton et al., 2002).

Another important factor which directly affects residual ortho-phosphorus removal is pH. Research has shown that the optimal pH range for iron is between 4 to 6 and the removal rate decreased dramatically once the pH was beyond the optimum range. For aluminum, a pH near 6 is optimum. When removing phosphorus with calcium, a higher pH near 9 usually promotes phosphorus removal (Diamadopoulos et al., 2013).

On the other hand, chemical precipitation has the disadvantages of relatively high electricity demand due to continuous chemical dosing, mixing and sludge removal requirements. It would be impractical to apply chemical dosing systems in areas without easy electricity access and human supervision.

2.5.7. BIOLOGICAL PHOSPHORUS REMOVAL

The research of biological phosphorus removal was established in the late 1950s. The most common biological technique is activated sludge in which the introduction of an anaerobic or anoxic zone at the front of an aerobic zone creates an environment for bacteria such as *Acinetobacter* to uptake 80-90% of the phosphorus in the aerobic tank with high phosphorus availability (Demirel et al., 2005). Biological P removal techniques typically have higher capital and operating costs compared to chemical precipitation, however, they have lower sludge disposal costs due to reduced sludge production. Biological P removal techniques are usually combined with chemical precipitation for municipal sewage.

The principle of biological P removal is to increase the minority amount of *Acinetobacter* by incorporating an anaerobic zone in front of the aeration tank. Under those circumstances, facultative anaerobic bacteria can produce low fatty acids, which are essential to *Acinetobacter* as a growth substrate. In the subsequent aerobic zone, the inorganic phosphates are uptaken by bacteria to form energy-rich polyphosphates, which are stored in the cells of the bacteria. The next cycle will start when *Acinetobacter* with polyphosphate is discharged with surplus sludge after the aerobic phase. However, it would be difficult to impossible to maintain the appropriate conditions in a passive system.

2.6. ADSORPTION

Adsorption is the transfer of atoms, ions and molecules from one substance such as gas, liquid and dissolved solid onto a surface under driving forces such as concentration gradient by diffusion. To have adsorption happen, the substance being attracted must have the affinity to the surface which represented as either Van der Waals forces with physisorption or chemical bonds (ionic or covalent bond) as chemisorption. In most water treatment scenarios, the most common adsorption is the mass transfer of substances from water onto a solid surface.

Physisorption is reversible and desorption will happen if the adsorbate phase concentration decreases, while chemisorption is typically non-reversible unless water chemistry is altered. Both physisorption and chemisorption are exothermic reactions and they give off 4-40 kJ/mol and over 200 kJ/mol, respectively.

The pore sizes of adsorbents determine the type of substance to be attracted to. Activated carbons have a wide range of pore sizes and are able to accommodate large

organic molecules such as natural organic matter (NOM) and synthetic organic compounds (SOCs) including pesticides, solvents and fuels. Some adsorbents have micro or even smaller pores and can only adsorb atoms and ions.

Surface area is key parameter that affects adsorbent's adsorption capacity. BET surface area analysis is a prevalent method in which nitrogen gas molecules are physically adsorbed on a solid surface and serves as the basis for the measurement of the specific surface area of materials. For common commercial porous water treatment adsorbents such as activated carbon, zeolite, and synthetic polymeric adsorbents, the specific surface area is significant large from 400 – 1500 m^2/g (John C Crittenden et al., 2012).

2.6.1. EQUATIONS OF ADSORPTION EQUILIBRIUM

For most cases in water treatment, the extent of concentrated adsorbate on adsorbent is usually a function of the residual concentration of adsorbate phase. The relationship is usually described as adsorption equilibrium isotherms. At the end of the equilibration period, the residual concentration in adsorbate phase is measured and the concentration of adsorbate adsorbed on the adsorbent is calculated using the mass balance expression.

$$q_e = \frac{V}{M}(C_0 - C_e) \qquad \text{Equation 2-3}$$

where $q_e =$ equilibrium adsorbent-phase concentration of adsorbate, mg adsorbarte/ g adsorbent;

$C_0 =$ initial aqueous-phase concentration of adsorbate, mg/L;

C_e = equilibrium aqueous-phase concentration of adsorbate, mg/L;

V = volume of aqueous phase, L;

M = mass of adsorbent, g.

The Langmuir adsorption isotherm

The Langmuir adsorption isotherm is used to describe the equilibrium between surface and solution as a reversible chemical equilibrium between species (Langmuir, 1918). The adsorbent surface is made up of fixed individual sites where molecules of adsorbate may be chemically bound. It can be expressed as:

$$q_A = \frac{Q_M b_A C_A}{1 + b_A C_A} \qquad \text{Equation 2-4}$$

where q_A = equilibrium adsorbent-phase concentration of adsorbate A, mg adsorbate/g adsorbent;

C_A = equilibrium concentration of adsorbate A in solution, mg/L;

Q_M = Maximum adsorbent-phase concentration of adsorbate when surface sites are saturated with adsorbate, mg adsorbate/g adsorbent;

b_A = Langmuir adsorption constant of adsorbate A, L/mg.

To rearrange to a linear form:

$$\frac{C_A}{q_A} = \frac{1}{b_A Q_M} + \frac{1}{Q_M} C_A \qquad \text{Equation 2-5}$$

The Freundlich adsorption isotherm

The Freundlich adsorption isotherm (Freundlich, 1906), originally proposed as an empirical equation, is used to describe the data for heterogeneous adsorbents:

$$q_A = K_A C_A^{1/n} \qquad \text{Equation 2-6}$$

where K_A = Freundlich adsorption capacity parameter, (mg/g) (L/mg)$^{1/n}$;

$1/n$ = Freundlich adsorption intensity parameter, unitless.

The linear form is

$$log(q_A) = log(K_A) + \left(\frac{1}{n}\right) log(C_A) \qquad \text{Equation 2-7}$$

2.7. A NOVEL MATERIAL: DIRECT-REDUCED IRON (DRI)

2.7.1. CHARACTERISTICS AND PRODUCTION

Direct reduced iron (DRI) is an intermediate product within the steel-making industry. It is produced from the direct reduction of iron ore (iron oxide) to high content metallic iron pellets by direct chemical reduction utilizing natural gas or coal (Stephenson and Smailer, 1980). Direct reduction competes with, and is an alternative to more conventional blast furnaces. Both DRI mills and blast furnace plants can process ore, to transform into a product which can then be processed further into steel. Worldwide, most of the iron-containing scrap material from a market share standpoint, feedstock entering EAFs is subdivided as follows: 80.0% scrap, 15.3% DRI/HBI products and 4.7% from blast furnaces (Gomes, 2016). The DRI production process typically produces DRI with an iron content in the 80-90% range (Anameric and Kawatra, 2007). The conversion of ore to metallic iron takes place under temperatures between 800 – 1200 °C, below the melting point of iron. Because of this, the direct reduction process is comparatively more energy efficient than conventional blast furnaces (Kirschen et al., 2011).

DRI has become an interesting alternative to conventional furnace methods of processing iron, as the initial capital investment (CAPEX) and operating costs (OPEX) of direct reduction plants are lower than integrated steel plants, and are more suitable for developing countries due to the ability to build “mini-mills”. Since the 1970s, the production of DRI has experienced major expansions in Australia, Europe, North America and Asia. India is now the World’s largest producer of DRI. Canada also has its place in

the steel industry, with 15 steel plants located in Alberta, Saskatchewan, Manitoba, Ontario and Québec (Environment and Climate Change Canada, 2013). There is only one direct-reduced plant in Canada, ArcelorMittal, which locates in Contrecoeur, Quebec.

During direct reduction process, the oxygen inherent to the iron oxide in the feed stock is removed from the system via reducing-gases, leaving the DRI produced with a similar but more porous physical form than the original iron oxide feed stock utilized. Thus, due to this porous structure, DRI is often called sponge iron. Figure 2.2 below illustrates the porous nature of DRI, via scanning electron microscope imaging of the surface of DRI pellets.

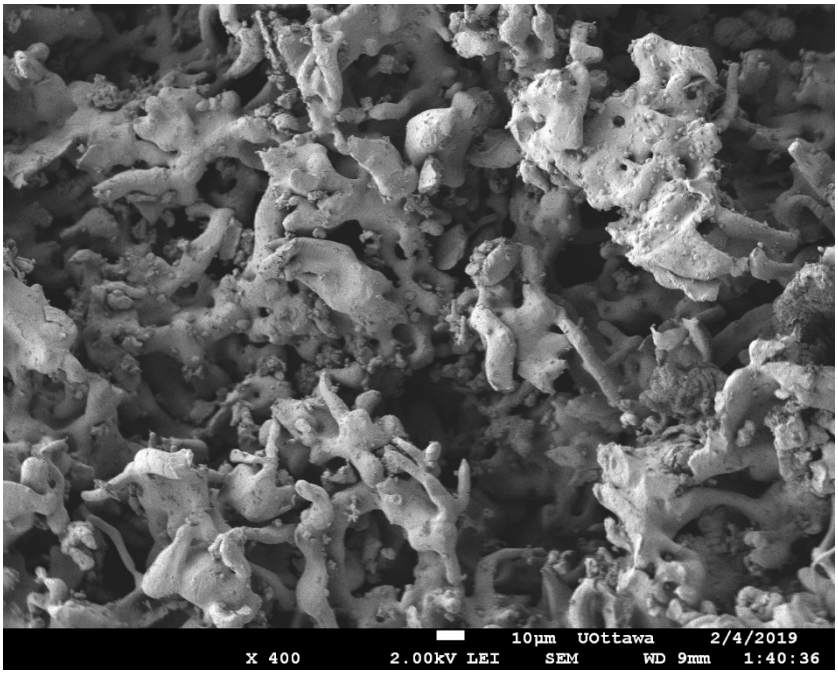

Figure 2.2. SEM imaging of the surface of DRI pellets, clearly showing the highly porous nature of the material.

Some of the physical and chemical properties of DRI are listed below, in Table 2.4.

Table 2.4. Physical and chemical characteristics of DRI (adapted from Anameric & Kawatra, 2007)

Characteristic	*Typical DRI values*
Density	1.5 – 4.0 g/cm^3
Bulk density	1.5 – 1.9 ton / m^3
Specific surface area (porosity)	0.5 – 4.0 m^2/g
% Metallic iron	90 – 95%
Degree of metallization	~ 85%

The physical and chemical stability of direct-reduced iron affects the handling, storage and transportation requirements of DRI. DRI has a re-oxidizing and self-heating tendency due to reductant state and low heat conductivity which will lead to exothermic reaction. It is possible for DRI to self-heat itself to the point of ignition if the DRI's thermal conductivity is low. Moisture can accelerate hot DRI's self-oxidation. In the exothermic reaction content, DRI is a strong reductant that reduces H^+ to H_2 and iron is oxidized into FeO. Hydrogen is highly explosive in the large range of 4% to 75% in air.

$$Fe + H_2O \rightarrow FeO + H_2$$ Equation 2-8

Some methods could be used to prevent this from happening during the shipping and storage by ventilation and inert gas sealing such as N_2 (Anameric and Kawatra, 2007). The hatches should be always kept clean, dry and watertight. The detecting measurement should be monitored during the shipping in terms of moisture content (< 1%), oxygen (< 5%), hydrogen (< 1%) and temperature (<65ºC) (Dutta and Sah, 2014). Also, the re-

oxidizing tendency of DRI decreases with increasing age. DRI should be naturally aged for at least 72 hours before shipping (Dutta and Sah, 2014).

A similar zero valent based media was investigated in the application of groundwater/contaminated land remediation as the reductant/sorbent to remove heavy metals and organic contaminants (Cundy et al., 2008; Kanel et al., 2007). However, the iron-based media has not been applied in P removal of wastewater.

2.7.2. WASTEWATER TREATMENT VIA DRI MEDIA

In the past decade, few studies investigated DRI as phosphorus retaining media from wastewaters. Xue et al. (2018) investigated adsorption isotherm and kinetic studies of DRI media, and in this study, the saturated adsorption capacity was predicted to be 3.25 mg P/g under neutral condition by Langmuir model. Xue et al. claimed that the maximum capacity was significantly improved under acidic solution ($pH \leq 4$). The BET surface area was found to be around 1.043 m^2/g. Wang et al. (2015) also conducted DRI media of enhanced phosphorus removal which was collaborated with microbiology studies. An over 90% of TP removal rate was achieved in this study with an influent TP of 8.08 mg P/L.

2.8. CONCLUSION

Phosphorus pollution in surface waters currently is and will continue to be one of the leading issues for surface water quality around the World for the foreseeable future. Humankind and its relationship with phosphorus is heavily intertwined. Our survival as a species depends on using phosphorus to sustain an increased crop yield to support an ever-increasing global population. The research in capturing and potentially reusing non-point

source phosphorus is sorely lacking as current methods generally focus on removal but not recovery. There is currently a fundamental lack of knowledge in phosphorus capture and reuse from agricultural and decentralized sites. The development of technologies and methods to recapture phosphorus will become increasingly important in the future as our ability to easily extract mineral phosphorus diminishes.

This manuscript will focus on the role of DRI as a potential reusable filter media to capture and reuse phosphorus due to its unique chemical characteristics. From the literature it is evident that DRI has similar, and hopefully superior working characteristics to that of other materials such as EAF slag.

DRI has, to the author's knowledge, has never been investigate directly in any water/wastewater treatment application for the removal of phosphorus. There are several research objectives which need to be investigated, including phosphorus removal capacity and kinetics of the media, influence of the media's surface geometry on removal, media life and time to reach saturation and phosphorus recovery methods from the media.

The use of DRI for phosphorus polishing or removal applications has not been explored in academia but should be investigated as a potentially promising material for phosphorus removal in passive filters.

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CHAPTER 3 : MATERIALS AND METHODS

3.1. EXPERIMENTAL DESIGN

In this study, direct-reduced iron (DRI) is investigated to evaluate its suitability as a phosphorus (P) retaining filter media. DRI was acquired from two different direct-reduction plants, in Gongyi City, Henan Province, PRC (Gongyi City Meiqi Industry Co., Ltd) and Contrecoeur, Québec, Canada (ArcelorMittal), respectively. An additional media, activated alumina (AA), was also acquired from Gongyi City Meiqi Industry Co., Ltd. This study is separated into several laboratory experiments. In the first set of experiments, synthetic wastewater containing P was utilized to conduct batch assays with increasing P concentration, in order to determine the media's maximum P removal capacity (media diameter 11 mm). In each batch assay, the time to reach saturation, the residual phosphorus and iron concentrations, the solid phase P concentration and solution pH were measured. Throughout these batch assays, the P retaining capacity of DRI and AA under specific conditions was investigated.

The second set of experiments consisted of two distinct column studies. The first set of columns were fed a synthetic wastewater containing P. The synthetic water column study consisted of operating four columns, three of which contained Gongyi City Meiqi Industry Co., Ltd DRI media with different nominal diameters (3.5 mm, 11 mm and 19 mm), while the fourth one contained AA (7.5 mm). The influent P concentration and hydraulic retention time of the columns were altered to explore the relationship between the P removal efficiency/P removal rate and the P loading rate. The second set of columns was dosed with municipal lagoon effluent. The real wastewater column study consisted of operating four columns, three of which contained a 50%/50% blend of P retaining material

and pea-stone, while the fourth one contained only pea-stone (as blank). These columns were fed municipal wastewater lagoon effluent collected from Casselman, Ontario, Canada, which had its P concentration augmented to 4.0 mg/L P.

Finally, a third set of experiments explored the potential for DRI media rejuvenation via chemical (acid) treatment with the quantity of P removed and recovered measured. Four types of regeneration reagents with multiple concentrations and regeneration times were applied in order to determine the optimal type of reagent, concentration and contact time.

3.2. MEDIA CHARACTERIZATION

3.2.1. ORIGIN OF MEDIA

In this study, two distinct direct-reduced iron samples were studied. The first sample was acquired from Gongyi City Meiqi Industry Co., Ltd's iron ore reduction plant (Gongyi City, Henan Province, PRC), and was available in three nominal diameters: 3.5 mm, 11 mm and 19 mm. This DRI will be annotated as DRI^1 throughout subsequent chapters. The second DRI sample was acquired from ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada, with an average diameter of 12.5 mm. This DRI will be annotated as DRI^2 throughout subsequent chapters.

During the batch assays, 11 mm diameter (Ø) DRI^1 media was investigated in terms of its phosphorus removal mechanisms and phosphorus removal capacity.

For fixed-bed column experiments, 3.5, 11 mm, 19 mm Ø DRI^1 media and 7.5 mm Ø activated alumina (also acquired from Gongyi City Meiqi Industry Co., Ltd) media were

utilized. In a second phase, the media were mixed with pea-stone gravel (Ø 10 mm) to form 50% (%v/v) pea-stone/adsorbent media blends, to investigate media filling percentage's effect on P removal efficiency. The pea-stone was acquired from King Packaged Materials Company (Oakville, Ontario, Canada).

A resume of the different assays and studies performed, along with media utilized is shown below in Table 3.1.

Table 3.1. Summary of media utilized in different assays and studies

Batch assays		Column experiment 1 (Synthetic wwt)		Column experiment 2 (Real wwt)	
Media	Diameter	Media	Diameter	Media	Diameter
DRI[1]	11 mm	DRI[1]	3.5 mm	DRI[1]	11 mm
			11 mm	DRI[2]	12.5 mm
			19 mm	AA	7.5 mm
		AA	7.5 mm	pea-stone	10 mm

DRI – direct-reduced iron; AA – activated alumina

DRI[1] – acquired from Gongyi City Meiqi Industry Co., Ltd in Gongyi City, Henan Province, PRC.

DRI[2] – acquired from ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada.

3.2.2. ELEMENTAL ANALYSIS OF THE MEDIA

The elemental analysis of the first DRI[1] was conducted at the Department of Earth and Environmental Sciences' geochemistry laboratories in the Advanced Research Complex at the University of Ottawa. This DRI was analyzed via ICP-OES utilizing an Agilent 5110 Synchronous Vertical Dual View (SVDV) (Santa Clara, CA, USA). Samples destined for ICP-OES analysis were finely ground using a mortar and pestle and triplicated,

prior to submittal to the laboratory. Information on the elemental composition of DRI[2] was provided by ArcelorMittal.

3.2.3. SPECIFIC SURFACE AREA OF MEDIA

The specific surface areas of the two types of DRI (DRI[1] and DRI[2)] and AA were measured at McGill University's Materials Characterization laboratory (Montreal, Québec, Canada) using a TriStar 3000 (Micromeritics Instrument Corp, Norcross, GA, USA). Brunauer-Emmett-Teller theory (BET) is an important analysis technique for the measurement of the specific surface area of materials. The BET model describes the multilayer adsorption, which is, a random distribution of sites covered by multiple adsorbate molecules. The concept of the theory is an extension of the Langmuir theory, from a theory for monolayer molecular adsorption, to multilayer adsorption.

3.2.4. SPECIFIC GRAVITY

The specific gravity was determined as per an adapted methodology of ASTM C127–07. Experiments were conducted at room temperature (23 ± 1°C) and were replicated five times. First, samples of media were dried at 105 °C for 3 hours. Afterwards, media samples were weighed using a Mettler Toledo AG285 digital analytical balance (Columbus, OH, USA) and the mass was recorded as M_{dry}. Samples were then submerged and suspended in a beaker filled with distilled water with fine fishing wire. The initial mass of the beaker and water was recorded ($M_{beaker+water}$) and the mass of the beaker, water and suspended media was also recorded, as M'. The specific gravity was then calculated using the equation below:

$$SG = \frac{\rho_{sample}}{\rho_{H_2O}} = \frac{M_{oven,dry}}{M' - M_{beaker,H_2O}}$$ Equation 3-1

SG : Specific gravity, unitless;

$M_{oven,dry}$: Mass of oven dried media samples, g;

M' : Mass of beaker and water inside with suspended media, g;

M_{beaker,H_2O}: Mass of beaker and water, g.

3.2.5. SURFACE MORPHOLOGY AND PHYSIC-CHEMICAL ANALYSIS

Both samples of DRI (DRI[1] and DRI[2]) and AA underwent Energy Dispersive X-ray Spectroscopy (EDS) measurements coupled with Scanning Electron Microscope (SEM) imaging, utilizing a JSM-7500F FESEM microscope (JEOL Ltd., Tokyo, Japan) at the Centre for Catalysis Research and Innovation (CCRI) at the University of Ottawa. SEM pictures were triplicated at each imaging magnification. Scanning Electron Microscope (SEM) imaging is performed utilizing an electron scanning microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental /chemical analysis of a sample. It relies on an interaction between X-ray excitation and a sample, and is capable of determining the elemental composition of specific points identified via SEM imaging.

3.3. BATCH ASSAYS

Batch assays were conducted to investigate the phosphorus removal capacity of DRI using 11 mm Ø DRI pellets. The removal capacity of 11 mm Ø DRI[1], mm Ø DRI[2] and 7.5 mm Ø AA were compared in 200 ppm P solutions (10 g media and 200 ml solution). All batch assays were triplicated and ran for over 9 days, where saturated conditions were obtained. All phosphorus concentrations stopped changing after 9 days.

11 mm Ø DRI[1] was further conducted in batch study with initial P concentrations ranging from 42 – 2829 mg P/L and 10 g DRI substrate (see Table 3.2). The synthetic P solutions utilized for the batch test experiments were prepared by weighing and dissolving appropriate quantities of ≥ 99% ACS-certified KH_2PO_4 (Fisher Scientific, Ottawa, Canada) into 200 ml of distilled water. The batch test experiments were conducted in 250 ml clean and dry LDPE (low-density polyethylene, 49.5 mm Ø diameter, 127 mm height) bottles. Residual P concentrations and pH were monitored throughout the process. Batch tests were conducted under agitated conditions using a New Brunswick™ Innova® 2000 orbital shaker (New Brunswick Scientific Co., Inc. Edison, NJ, USA) set at 117 rpm.

Table 3.2. Batch test initial phosphorus concentrations with 10 g DRI

Batch study initial P concentration
10 g DRI
42.1
83.4
139.5
271.4
377.2
580.7
920.1
1,327.2
1,637.8
2,222.5
2,731.1
2,829.2

Phosphorus retaining capacity from batch assays are calculated as below:

$$q = \frac{V}{M}(C_0 - C_e) \qquad \text{Equation 3-2}$$

where q =phosphorus retaining capacity (mg P/g media);

C_0 =initial P concentration (mg/L);

C_e =effluent/equilibrium P concentration (mg/L);

V =volume of liquid (L);

M =mass of media added (g).

3.4. COLUMN TESTS

Laboratory-scale columns were investigated in terms of the influence of filter media mean diameter and hydraulic retention time on phosphorus removal performance.

3.4.1. SYNTHETIC WASTEWATER COLUMNS

3.5, 11 mm and 19 mm DRI[1] and 7.5 mm activated alumina was utilized in four identical, 100 mm dia. by 317.5 mm cylindrical columns, as seen in Figure 3.1. The synthetic phosphorus influent was stored in a 300 L plastic bin, and based on the flowrate, the frequency of making feed ranges from 1.5 days to 1 week. Synthetic influent water with concentrations of 2.0, 4.0, 6.0, 8.0 and 10.0 mg P/L was dosed to the columns utilizing a Cole-Parmer Masterflex peristaltic pump (Vernon Hills, IL, USA) at flow rates of 1.4, 2.8, 4.2, 8.4 and 30 ml/min (corresponding to approximate hydraulic retention times (HRT) of 19, 9.5, 6.3, 3 and 0.5 hrs) in an upflow configuration, for a total of 300 + days. The hydraulic retention time was designed to be below 24 hours based on similar literature values and was modified based on experimental performance. Samples were collected every 0.5 to 4 days depending on the flow rate. Samples were triplicated once a week.

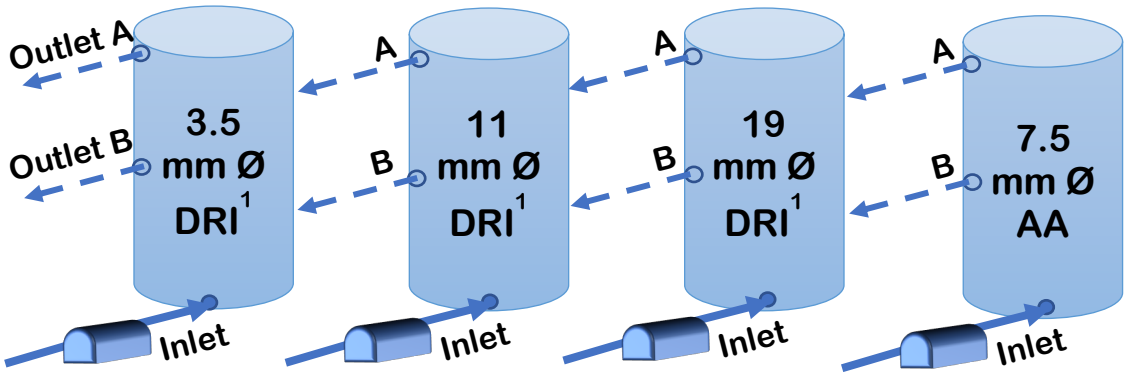


Figure 3.1. Experimental setup with four columns during the first set of column experiments, with synthetic wastewater.

Each column had two sample ports (Outlets A & B). Outlet A was situated at the very top, and Outlet B in the middle of each column. Outlet A, at the top, was always open allowing water to freely flow out of the column while Outlet B, in the middle, was only opened while a sample was being collected. A summary of the influent concentration and flowrate schedule is presented below in Table 3.3. The running time under each operational condition varies and all provided sufficient time for column effluent reaching steady state. Experiment results showed that it required less than 1 day to reach effluent equilibrium.

Table 3.3. Column test duration with varying influent concentrations (2 – 10 mg P/L) and HRTs (0.6 – 19.4 h)

	Column flowrate and HRT range				
Influent concentration	**1.4 ml/min (13.2 – 19.4 h)**	**2.8 ml/min (6.6 – 9.7 h)**	**4.2 ml/min (4.4 – 6.5 h)**	**8.4 ml/min (2.2 – 3.2 h)**	**30 ml/min (0.6 – 0.9 h)**
2 mg P/L	99 days	104.7 days	34 days	10 days	12 days
4 mg P/L	5 days	-	5 days	-	9 days
6 mg P/L	6 days	-	5 days	-	6 days
8 mg P/L	5 days	-	4 days	-	4 days
10 mg P/L	5 days	-	4 days	-	4 days

3.4.2. LAGOON EFFLUENT COLUMNS

DRI[1], DRI[2], AA and pea-stone were utilized to fill four identical (Figure 3.2), 100 mm dia. x 317.5 mm columns. The first three columns had 50/50% v/v blends of active phosphorus retaining material and pea-stone, in order to investigate the effect on performance of less active media with same retention time. The fourth column was filled with 100% pea-stone, to act as a blank column. DRI[1], DRI[2] and AA with an average nominal diameter of 11, 12.5 and 7.5 mm diameter, respectively, were utilized in this set of column assays. Effluent collected from the Casselman, ON municipal wastewater lagoon was augmented with <99% ACS-certified KH_2PO_4 up to a P concentration of ~ 4.0 mg/L P. The lagoon effluent was collected every 4 days to 1 week depending on the column flow rates and the water was storage in a 200 L plastic container. The average lagoon effluent characteristics were 12.2 mg TSS/L and 55.4 mg sCOD/L. The augmented lagoon effluent was dosed through the columns with a Cole-Parmer peristaltic pump. The columns were operated as upflow columns, with the effluent leaving at the top of the columns.

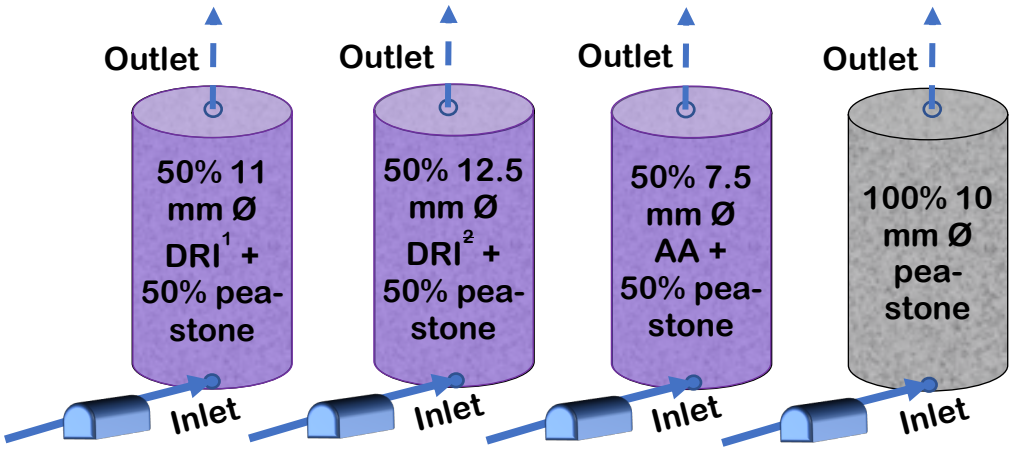


Figure 3.2. Experimental setup with four columns during the second set of column experiments, with augmented lagoon effluent.

The columns were operated with flows of 30 ml/min, 15 ml/min and 8 ml/min at a temperature of 23 ± 0.5ºC, representing HRTs of 0.3 – 0.65 h, 0.61 – 1.3 h and 1.1 – 2.3 h, based on media porosity. The columns were then brought into a walk-in refrigerator kept at 4 ± 0.5ºC, and tests were then performed at a flowrate of 8 ml/min. The hydraulic retention times in this set of assays ranged from 1.1 h - 2.3 h. Samples were collected daily and stored in 50 ml centrifuge tubes at 4 °C. Samples were triplicated once a week. Phosphorus analysis was generally conducted within 12 hrs of sample collection. A summary of the flow conditions is presented below in Table 3.4.

Table 3.4. Summary of the column operating conditions for the second set of column experiments (Influent P = 4 mg/L)

	23 ± 0.5ºC			**4 ± 0.5ºC**
Flow	30 ml/min	15 ml/min	8 ml/min	8 ml/min
HRT	(0.3 – 0.65 h)	(0.61 – 1.3 h)	(1.1 – 2.3 h)	(1.1 – 2.3 h)
Duration	12 days	9 days	7 days	7 days

3.5. WATER ANALYTICAL METHODS

3.5.1. SOLUBLE REACTIVE PHOSPHORUS

The soluble reactive phosphorus concentration of all samples was measured as per Standard Methods 4500-P D, using a HACH DR5000 UV-VIS Spectrophotometer (Loveland, CO, USA), with a 5 cm cuvette and wavelength 690 μm. Prior to testing, samples appeared as yellow color. Then the samples were fully mixed and were filtered through a 0.45 μm syringe filter where the liquid appeared transparent. In between readings, the cuvette's inner and outer walls were sprayed with distilled water with a spray bottle filled with distilled water. The cuvette was then preconditioned with the upcoming

sample by filling it up with the reacted sample, emptied into a liquid waste container and then filled again with the same sample. The cuvette was stored in a beaker containing distilled water while was not in use.

3.5.2. TOTAL PHOSPHORUS

The soluble reactive phosphorus concentration of all samples was measured as per Standard Methods 4500-P D, using a HACH DR5000 UV-VIS Spectrophotometer (Loveland, CO, USA), with a 5 cm cuvette. Samples were digested prior to testing by adding 2.0 ml 30% sulfuric acid solution and 0.4 g potassium persulfate to 50 ml of sample and autoclaving at 120 ºC for 30 mins. The samples were then re-diluted up to 50 ml using distilled water. In between readings, the cuvette's inner and outer walls were sprayed with distilled water with a spray bottle filled with distilled water. The cuvette was then preconditioned with the upcoming sample by filling it up with the reacted sample, emptied into a liquid waste container and then filled again with the same sample. The cuvette was stored in a beaker containing distilled water while was not in use.

3.5.3. SOLUBLE CHEMICAL OXYGEN DEMAND

The chemical oxygen demand concentration of all samples was measured following the HACH Method 8000 (equivalent to Standard Methods 5220 D). Prior to testing, samples were fully mixed and were filtered through a 0.45 μm syringe filter. 2.0 ml of filtered sample was then pipetted from the container and into a HACH COD LR vial. A HACH DRB200 reactor/digester was preheated to 150 °C prior to the start of the experiment and utilized to digest the samples for a period of two hours. After 140 minutes elapsed, the samples were then removed from the digester and left to cool to ambient

temperature in a test tube rack. Samples were then wiped down and read in a HACH DR 5000 spectrophotometer using the 430 COD LR program to obtain the soluble chemical oxygen demand concentration.

3.5.4. SOLUBLE IRON

The soluble iron concentration of all samples was measured as per EPA Method 7000B. Adequate quantities (10 - 50 ml) of samples were fully mixed and filtered through a 0.45 μm syringe filter. An appropriate quantity of concentrated nitric acid was added to every sample in order to maintain a 2% nitric acid concentration in the samples, to convert insoluble metal into their nitrate salts, which are highly soluble. Samples were then analyzed for iron concentration utilizing a PerkinElmer PinAAcle Flame Atomic Absorption Spectrometer (Waltham, MA, USA) Iron standards (1.0 mg Fe/L, 3.0 mg Fe/L and 10.0 mg/L) were run through the instrument prior to testing.

3.5.5. TOTAL IRON

The total iron concentration of all samples was measured as per EPA Method 7000B. The determination of total iron required digestion of the samples, which was performed as per ASTM D1971-16. 25.0 ml samples were fully mixed and 0.1 ml of concentrated nitric acid was added to the samples. Afterwards, 0.5 ml of concentrated HCl was added to every sample and they were then shaken vigorously. Samples were then digested at 65°C in an oven over a period of 8 hours and then left to cool to room temperature. Samples were then analyzed for iron concentration utilizing a PerkinElmer PinAAcle Flame Atomic Absorption Spectrometer (Waltham, MA, USA) Iron standards (1.0 mg Fe/L, 3.0 mg Fe/L and 10.0 mg/L) were run through the instrument prior to testing.

3.5.6. PH DETERMINATION

The pH of all samples was measured with a HACH HQ40d pH meter (Loveland, CO) with a PHC201 pH probe (Loveland, CO). The pH probe was calibrated prior to use with three buffer solutions with standard pH values of 4.01, 7.00 and 10.01. A distilled water spray bottle and delicate task wipes were used to rinse and dry the probe's glass electrode between every measurement. In between measurements, the pH probe was immediately stored in a 3N potassium chloride solution.

3.5.7. CONDUCTIVITY DETERMINATION

The conductivity of all samples was measured with a VWR sympHony B40PCID conductivity meter (Radnor, United States) with a VWR conductivity probe (Radnor, PA, USA). The conductivity probe was calibrated prior to use with conductivity standard of 100 μS/cm and 12.89 mS/cm. A distilled water spray bottle and delicate task wipes were used to rinse and dry the probe's electrode between every measurement. In between measurements, the pH probe was immediately stored in a KCl solution.

3.5.8. STATISTICAL ANALYSIS

Statistical analysis techniques were employed to ensure statistical relevance of data. During the batch assays, all samples were in triplicated to reduce the error caused by uneven specific surface area of the media and higher dilution factors (200, 400, 600). For column studies, samples were triplicated once per week. In addition, a regression analysis was performed with the linearized Langmuir and the Freundlich isotherm to predict the maximum phosphorus capacity per surface area/mass.

3.6. COLUMN TRACER STUDY

Potassium Bromide (KBr) was utilized as salt tracer to examine the hydraulic conditions of the reactor columns and to identify if short circuiting was occurring. Furthermore, the salt tracer was also utilized to verify the calculated hydraulic retention time. A salt solution containing 3000 mg KBr/L (~3.59 MS/cm) was utilized as a tracer agent. Initial background conductivity was determined to be ~41.6 μm/cm. During the tracer test, the columns' effluent conductivity was tested every 40 mins over a 25 hours period, until the effluent conductivity reached the influent conductivity.

3.7. MEDIA REGENERATION ASSAYS

Different types and concentrations of regeneration solutions were investigated during the regeneration assays to identify an optimum regeneration solution, concentration and appropriate regeneration time to optimize phosphorus recovery from the media and P removal capacity recovery of the DRI media. Two concentrations of ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3$), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) solutions were utilized during the first regeneration assay to determine which was the most favorable regeneration reagent. Detailed information is shown in Table 3.5 below.

Table 3.5. Preliminary trials with four regeneration liquids at varying concentrations

Regeneration Liquid	Concentration	Regeneration solution volume (ml)	Mass of saturated media (g)	Time (h)
$FeCl_3$	0.023 M Fe^{3+}	100	10	48
	0.048 M Fe^{3+}	100	10	48
$Fe_2(SO_4)_3$	0.026 M Fe^{3+}	100	10	48
	0.052 M Fe^{3+}	100	10	48
HCl	0.4 N H^+	100	10	48
	0.8 N H^+	100	10	48
H_2SO_4	1.2 N H^+	100	10	48
	2.2 N H^+	100	10	48

Prior to regeneration, 10 g of virgin media was saturated in a 200 ml solution containing 200 mg/L P for approximately 10 days. This phosphorus retention capacity was recorded as q_0. After this, the media was immersed in 100 ml of regeneration solution for a period of 48 hours. Afterwards, the media was once again immersed in a 200 ml solution containing 200 mg/L P for approximately 10 days until it became saturated once more. This phosphorus retention capacity was recorded as $q^{'}$. To further investigate the impact of concentration and time on the regeneration recovery rate, the reagent type for the regeneration solution was narrowed down to HCl and H_2SO_4. Concentrations of 0.05 N, 0.1 N, 0.15 N and 0.2 N were analyzed with regeneration times of 3 hrs, 10 hrs and 24 hrs. 100 ml of 200 ppm phosphorus solutions were used before and after regeneration to saturate the media. Detailed information is listed below in Table 3.6:

Table 3.6. Regeneration trials with varying normality of HCl and H_2SO_4

Type	Concentration (N)	Volume (ml)	Rejuvenation Time (h)		
HCl	0.05	30	3	10	24
	0.10	30	3	10	24
	0.15	30	3	10	24
	0.20	30	3	10	24
H_2SO_4	0.05	30	3	10	24
	0.10	30	3	10	24
	0.15	30	3	10	24
	0.20	30	3	10	24

3.8. REFERENCE

APHA, WEF, A., (2012), *Standard Methods for the Examination of Water and Wastewater, 22nd Edition*. ed. APHA, WEF, AWWA, Washington, D.C.

ASTM C127-07, (2007), *Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate*, ASTM International, West Conshohocken, PA, www.astm.org

ASTM D1971-16, (2016), *Standard Practices for Digestion of Water Samples for Determination of Metals by Flame Atomic Absorption, Graphite Furnace Atomic Absorption, Plasma Emission Spectroscopy, or Plasma Mass Spectrometry*, ASTM International, West Conshohocken, PA, www.astm.org

CHAPTER 4 : INVESTIGATION OF PHOSPHORUS REMOVAL CAPACITY UTILIZING DIRECT-REDUCED IRON (DRI): BATCH STUDIES AND MEDIA REGENERATION

4.1. SETTING THE CONTEXT

The manuscript presented in Chapter 4 is titled *Investigation of phosphorus removal capacity utilizing direct-reduced iron (DRI): Batch studies and media regeneration* by H. Qin, C. Kinsley, and P. M. D'Aoust. This manuscript firstly characterizes direct-reduced-iron (DRI) and activated alumina (AA) to determine its elemental composition, density and specific gravity, morphology and specific surface area. Secondly, this manuscript investigates the maximum phosphorus retaining capacities of DRI and AA based on P concentration in a series of batch assays with synthetic P solutions. Finally, media (DRI) regeneration and phosphorus recovery by chemical treatment was investigated.

4.2. ABSTRACT

Phosphorus is a biologically active compound which has been intensely extracted and utilized by humans to enhance agricultural productivity. However, when allowed to enter natural aquatic environments in excess quantity, it can have deleterious effects on water quality and thus human health. This study characterised and evaluated the performance of direct-reduced iron (DRI), a novel phosphorus removal filter material. Preliminary jar tests run at 200 mg P/L compared DRI to activated alumina (AA) and demonstrated lower P removal capacity to AA on a mass basis but higher capacity on a volume basis. Further jar tests investigated DRI capacity with phosphorus concentrations and demonstrated the maximum phosphorus removal capacity of DRI with influent concentration. The Langmuir isotherm was shown to effectively model maximum adsorption capacity and equilibrium concentration. The DRI P removal capacities were shown to have higher removal capacity at similar initial P concentrations to commonly used P adsorbent materials reported in literature.

It was hypothesised that DRI removes phosphorus through two primary mechanisms: adsorption and crystal formation. Jar test isotherms suggest adsorption as a mechanism, while crystallization of iron phosphate was observed under SEM imaging and XRD. Residual soluble iron was shown to be within typical ranges found in the natural environment. Several experiments were conducted to optimize the regeneration of saturated DRI media. Fe^{3+} and H^{+} were both shown to promote regeneration of P removal capacity of the media with 0.05 M Fe^{3+} or 0.4 N H^{+} achieving 100% capacity recovery. P mass recovery from the media was only accomplished by H^{+} with a maximum 37.6% of P mass recovery achieved with 1.2 N H^{+} acid solution.

4.3. INTRODUCTION

Phosphorus (P) is frequently a limiting nutrient for plant, algae, macrophyte and microorganism growth in aquatic environments. In water and wastewater, the most commonly encountered form of P is orthophosphate (PO_4^{3-}-P), causing it to be the most commonly targeted P-containing compound for removal (Carpenter, 1985). North American waters are highly impacted by nutrients, with studies suggesting that up to 50% of lakes and 60% of rivers are affected by an excess in nutrient input. This has led to eutrophication becoming a topic of great concern in both the United States and Canada (Beauchemin and Simard, 2011; Parry, 1998; USEPA, 2002). The agricultural industry is one of the largest contributors to nutrient pollution in surface waters across the world. It is estimated that internationally, the livestock industry alone was responsible for contributing to between 14 – 72% and 32 – 94% of the nitrogen (N) and P entering the natural environment, respectively (FAO and LEAD, 2006). Other sources of phosphorus impacting surface waters include industry, stormwater management systems, centralized and decentralized domestic wastewater treatment systems. Chemical precipitation of P in wastewater with metal salts remains the preferred method for P removal due to its effectiveness (Jiang and Graham, 1998), however, the operation of coagulation and sludge management systems is impractical for diffuse sources of pollution such as agricultural drainage or stormwater runoff. In these cases, as well as with low-flow decentralized wastewater applications, wetlands or filter-type removal systems may be preferable and/or more cost effective. Wetland studies have generally demonstrated a clear ability to remove both N & P (Kovacic et al., 2010), however, their performance has been found to be highly sensitive to retention time (Woltemade, 2000), wetland maintenance schedule (Kadlec,

2016) and general physicochemical characteristics of the soil, sediment and water volume (Ready et al., 1999). Aside from wetlands, filter-type facilities utilizing iron or metal-rich aggregate or media such as slag (Claveau-Mallet et al., 2012; Okochi and McMartin, 2011), natural minerals (Bellier et al., 2006; Gustafsson et al., 2008) or zeolites (Xie et al., 2015) have also had success in capturing and retaining phosphorus. In this paper, the P-retention potential of a novel, previously untested iron-rich media, direct-reduced-iron (DRI), as well as activated alumina (AA), which is known for extraordinarily high specific surface area, were studied. DRI is an intermediate product in the steel industry, produced from iron ore in direct-reduction steel plants, and is a porous, iron-rich aggregate. Activated alumina is synthetic, highly porous material, and is largely composed of alpha-A_2O_3, which is stable and chemically inactive (Saussol, 1959).

4.4. MATERIALS AND METHODS

4.4.1. MEDIA

In this study, a preliminary screening test was performed to compare three types of media: DRI[1], DRI[2] and AA as described in Table 4.1. DRI[1] and AA were acquired from Gongyi City Meiqi Industry Co., Ltd's reduction plant (Gongyi City, Henan Province, China). DRI[2] was acquired from ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada.

Table 4.1. Media dimension and location of origin

Media	DRI[1]	DRI[2]	AA
Diameter	11 mm	12.5 mm	7.5 mm
Location of origin	Gongyi City Meiqi Industry Co., Ltd's reduction plant (Gongyi City, Henan Province, PRC)	ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada	Gongyi City Meiqi Industry Co., Ltd's reduction plant (Gongyi City, Henan Province, PRC)

4.4.2. MEDIA CHARACTERIZATION

Three filter media were characterized for density, surface morphology and chemical composition. Specific gravity was determined as per ASTM C127– 07. The specific surface area was determined via Brunauer-Emmett-Teller (BET) analysis utilizing a TriStar 3000 (Micromeritics Instrument Corp, Norcross, GA, USA) at McGill University's Materials Characterization laboratory (Montreal, QC, Canada).

Morphological and chemical information on the DRI media was obtained via Energy Dispersive X-ray Spectroscopy (EDS) coupled with Scanning Electron Microscope (SEM) imaging, utilizing a JSM-7500F FESEM microscope at the Centre for Catalysis Research and Innovation (CCRI) at the University of Ottawa (Ottawa, Ontario, Canada). Finally, information on the complete chemical composition of DRI was determined via ICP-OES utilizing a 5110 SVDV (Agilent, United States) at the University of Ottawa's Advanced Research Complex.

4.4.3. BATCH ASSAYS

Preliminary batch tests were conducted by using 11 mm Ø DRI[1] pellets (Gongyi City, PRC), 12.5 mm Ø DRI[2] pellets (Contrecoeur, Québec, Canada) and 7.5 mm Ø activated alumina (Gongyi City, PRC) in 250 ml, clean, dry LDPE (low-density polyethylene) bottles with 10 g substrate, 200 ml solution and an initial phosphorus concentration 200 mg/L. All tests were triplicated and were shaken on a New Brunswick™ Innova® 2000 orbital shaker (Edison, NJ, USA) at 117 rpm.

Based on the preliminary study results, DRI[1] pellets were chosen to be further investigated under various P concentrations. Assays had 10 g DRI[1] media exposed to solutions of varying phosphorus concentrations, ranging from 42 – 2829 mg P/L (see Table 4.2), to reach the maximum capacity for the unit mass of the media. This was performed to investigate the relationship of P removal capacity of unit mass media with P concentration. P concentrations were recorded daily for up to 10 days when the media became saturated.

Table 4.2. Concentrations of phosphorus solutions for the batch assays with 10 g of DRI[1]

Initial P concentrations (mg P/L)
10 g DRI
42.1
83.4
139.5
271.4
377.2
580.7
920.1
1,327.2
1,637.8
2,222.5
2,731.1
2,829.2

4.4.4. DATA ANALYSIS METHODS

The linearized Langmuir and Freundlich isotherms, which are shown as **Error! R eference source not found.**) and **Error! Reference source not found.**) were used to model and describe the jar test results.

The Linearized Langmuir adsorption isotherm

$$\frac{C_A}{q_A} = \frac{1}{b_A Q_M} + \frac{1}{Q_M} C_A \qquad \text{Equation 4-1}$$

where $q_A =$ equilibrium adsorbent-phase concentration of adsorbate A, mg adsorbate/g adsorbent

$C_A =$ equilibrium concentration of adsorbate A in solution, mg/L

Q_M = Maximum adsorbent-phase concentration of adsorbate when surface sites are saturated with adsorbate, mg adsorbate/g adsorbent

b_A = Langmuir adsorption constant of adsorbate A, L/mg

The Linearized Freundlich adsorption isotherm

$$log(q_A) = log(K_A) + \left(\frac{1}{n}\right) log(C_A) \qquad \text{Equation 4-2}$$

where K_A = Freundlich adsorption capacity parameter, (mg/g) $(L/mg)^{1/n}$;

$1/n$ = Freundlich adsorption intensity parameter, unitless;

q_A = equilibrium adsorbent-phase concentration of adsorbate A, mg adsorbate/g adsorbent;

C_A = equilibrium concentration of adsorbate A in solution, mg/L.

Three parameters were used to measure the quality of fitness of two models: sum of squares (S_r), residual mean square (MS), and residual plots.

Sum of squares (S_r)

$$S_r = \sum_{i=1}^{n} (y_i - f[x, \theta])^2 \qquad \text{Equation 4-3}$$

where y_i = experimental P removal capacity (mg P/g);

$f[x, \theta]$ = predicted P removal capacity (mg P/g).

Residual mean squares (MS)

$$MS = \sqrt{\frac{S_r}{n-(p+1)}} \qquad \text{Equation 4-4}$$

where $n =$ the number of data points;

$p =$ the number of parameters (coefficients) within the model.

Residual plots

Plot the residuals (i.e., $y_i - f[x, \theta]$) versus the values of the independent variables (x). The residual plot will be determined visually if the residuals are randomly distributed.

P retention capacity

$$q = \frac{V}{M}(C_0 - C_e) \qquad \text{Equation 4-5}$$

where q =phosphorus retaining capacity (mg P/g media);

C_0 =initial P concentration (mg/L);

C_e =effluent/equilibrium P concentration (mg/L);

V =volume of liquid (L);

M =mass of media added (g).

4.4.5. WATER QUALITY ANALYTICAL METHODS

Total phosphorus and orthophosphates were measured as per SM 4500 P-D (APHA, WEF, 2012) (stannous chloride) under wavelength 690 μm, using a HACH DR6000 UV-VIS spectrophotometer (Loveland, CO, USA) coupled to a 50 mm quartz cuvette. pH measurements were performed using a HACH HQ40D handheld meter coupled to a PHC101 pH probe (Loveland, CO, USA).

Soluble and total iron concentrations were measured as per EPA Method 7000B (USEPA, 2007) using a PerkinElmer PinAAcle 500 Flame Atomic Absorption Spectrometer (Waltham, MA, USA).

The precipitate was separated from the solution by centrifuging at 1000 ppm using 25 ml centrifuge tubes. The precipitate was then dried at 35 °C over night and taken to X-ray Core Facility at University of Ottawa using a Rigaku Ultima IV diffractometer (Tokyo, Japan) for component identification.

4.4.6. MEDIA REGENERATION AND PHOSPHORUS RECOVERY

$FeCl_3$, $Fe_2(SO_4)_3$, HCl and H_2SO_4 solutions of various concentrations were utilized in the regeneration trial. Detailed information of all regeneration assays including regenerant concentration, volume, and regeneration time are summarized below in Table 4.3. For each individual assay, 10 grams of DRI saturated in 200 mg P/L solution was used.

Table 4.3. The concentration, volume and time of the regenerant solutions in media rejuvenation.

Regenerants	Concentration	Volume	Regeneration time
$FeCl_3$	0.023 M Fe^{3+}	100 ml	48 hr
	0.048 M Fe^{3+}	100 ml	48 hr
$Fe_2(SO_4)_3$	0.026 M Fe^{3+}	100 ml	48 hr
	0.052 M Fe^{3+}	100 ml	48 hr
HCl	0.4 N H^+	100 ml	48 hr
	0.8 N H^+	100 ml	48 hr
	0.05 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.10 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.15 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.20 N H^+	30 ml	3 hr, 10 hr, 24 hr
H_2SO_4	1.20 N H^+	100 ml	48 hr
	2.20 N H^+	100 ml	48 hr
	0.05 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.10 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.15 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.20 N H^+	30 ml	3 hr, 10 hr, 24 hr

In the second part of this trial, the phosphorus recovery rate was investigated in each type and concentration of the regeneration solutions by quantifying ortho-phosphorus and total phosphorus mass in the regenerant solution after the respective regeneration time. Experimental details are described in Table 4.4.

Table 4.4. The concentration, volume and time of the regenerant solutions in phosphorus recovery.

Regenerants	**Concentration**	**Volume**	**Regeneration time**
$FeCl_3$	0.023 M Fe^{3+}	100 ml	5 min, 30 min, 180 min
$Fe_2(SO_4)_3$	0.026 M Fe^{3+}	100 ml	5 min, 30 min, 180 min
HCl	0.4 N H^+	100 ml	5 min, 30 min, 180 min
	0.05 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.10 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.15 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.20 N H^+	30 ml	3 hr, 10 hr, 24 hr
H_2SO_4	1.20 N H^+	100 ml	5 min, 30 min, 180 min
	0.05 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.10 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.15 N H^+	30 ml	3 hr, 10 hr, 24 hr
	0.20 N H^+	30 ml	3 hr, 10 hr, 24 hr

4.5. RESULTS AND DISCUSSION

4.5.1. MEDIA CHARACTERISTICS

The physical characteristics and chemical compositions of the tested media are outlined below in Table 4.5 and Table 4.6, respectively.

Table 4.5. Characteristics of filter media

Material	Standard deviation (mm)	Location of origin	Bed density (kg/m^3)	Density (g/cm^3)	Specific area (m^2/g) (Avg. ± SD)	Bed porosity (%)
3.5 mm Ø DRI[1]	0.70	Gongyi City, Henan Province, PRC	1283	3.76	0.34 ± 0.12	65.9
11 mm Ø DRI[1]	2.03		1357	2.82	0.32 ± 0.22	51.9
19 mm Ø DRI[1]	5.85		1671	3.08	0.33 ± 0.17*	45.8
7.5 mm Ø AA	0.32		739	1.34	250.2 ± 37.7	44.8
12.5 mm Ø DRI[2]	1.24	Contrecoeur, Quebec, Canada	1653	2.93	0.27 ± 0.04	41.1

DRI – direct-reduced iron; AA – activated alumina

DRI[1] – acquired from Gongyi City Meiqi Industry Co., Ltd in Gongyi City, Henan Province, PRC.

DRI[2] – acquired from ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada.

*0.33 ± 0.17 was calculated as average value of 3.5 and 11 mm DRI samples

The specific area obtained with the BET analysis demonstrates similar average values of specific surface area (0.34, 0.32 and 0.27 m^2/g) among DRI media. These values are a little lower than those of the research of Anameric and Kawatra, (2007), who reported an average surface area 0.5 - 4.0 m^2/g. The specific area in the PRC DRI[1] media was found to be more variable than the Contrecoeur DRI[2] media, likely due to differences in the production method and reduction conditions at different plants. The DRI media (over 87%

iron) has a significantly lower specific density (2.83 – 3.76 g/cm^3) than bulk iron (7.87 g/cm^3) (Elert, 2007), highlighting the material's significant porosity (52.2 – 64.0%). The specific density is slightly lower than traditional values for DRI produced via the MIDREX® process (3.40 – 3.60 g/cm^3) (Midrex, 2015), but in line with findings of other studies on DRI (1.5 – 4.0 g/cm^3, 2.93 g/m^3) (AbdElmomen, 2013; Anameric and Kawatra, 2007). Activated alumina is known for high specific surface area which can reach over 200 m^2/g (Jovanović et al., 1992). The activated alumina was analysed to have 250.2 m^2/g specific surface area with 15.1% error, highlighting its extremely small pores.

Elemental analysis via ICP-OES revealed that DRI[1] is 87.48 ± 0.97% iron. The elemental composition information of DRI[2] was provided by its supplier ArcelorMittal, which is 92.2 ± 2.1% Fe. Activated alumina constitutes 100% Al_2O_3. The detailed results of the elemental analysis for the three media are shown in Table 4.6.

Table 4.6. Elemental analysis of DRI[1] and DRI[2]

DRI[1] (ICP-OES)*	**Element**	**Al**	**Ca**	**Cr**	**Fe**	**Mn**	**Na**	**Ni**	**Si**	**Mg**
	Concentration (%)	0.10	0.16	0.02	87.48	0.37	0.05	0.02	0.02	0.02
DRI[2] (ArcelorMittal)*	**Element**	**Fe**	**O**	**C**						
	Concentration (%)	92.18	2.55	1.80						
AA	**Composition**	Al_2O_3								

*The elemental composition of DRI[1] from ICP-OES analysis does not quantify O and C elements.
**The data of DRI[2] was provided by ArcelorMittal.

Contrary to many other P-retaining media, DRI does not have significant calcium content due to its modern manufacturing process, in which the oxygen is driven off by adding reduction gas CO or coal. In conventional smelting iron making process, oxygen is removed by adding lime $CaCO_3$ which reacts with impurities such as silicon, sulfur and excess carbon. The conventional steel manufacturing by-product such as slag, which contains a quantity of $CaCO_3$ and $Ca(OH)_2$ due to the lime addition during the steel making process, has been largely used in P retaining filters (Al Timimi, 2015). Instead, direct-reduced iron is manufactured as an intermediate step in the steel manufacturing process. Therefore, the main component in direct-reduced iron is metallic iron (approximately 85%) (Anameric and Kawatra, 2007).

SEM images of the materials are presented in Figure 4.1. It is observed that DRI^1 (A) has the largest pore size of about 15 μm, the pore size of DRI^2 (B) is around 1 – 2 μm while the AA (C) has very small pore size < 1 μm which are not clear on the SEM photo. Pore sizes below 0.03 μm are non-visible under SEM and can adsorb ions and small molecular species while the pore sizes ranging from 20 – 50 μm, has the potential to retain larger organic compound such as natural organic compound (NOCs) and synthetic organic compound (SOCs) (John C Crittenden et al., 2012). DRI^1 and DRI^2 have similar surface morphology but different pore sizes which is likely caused by differences in manufactural procedures. During the production of DRI, oxygen is evacuated from the mother material with reducing gases, producing a sponge-like structure. Therefore, another name of direct-reduced iron is sponge iron.

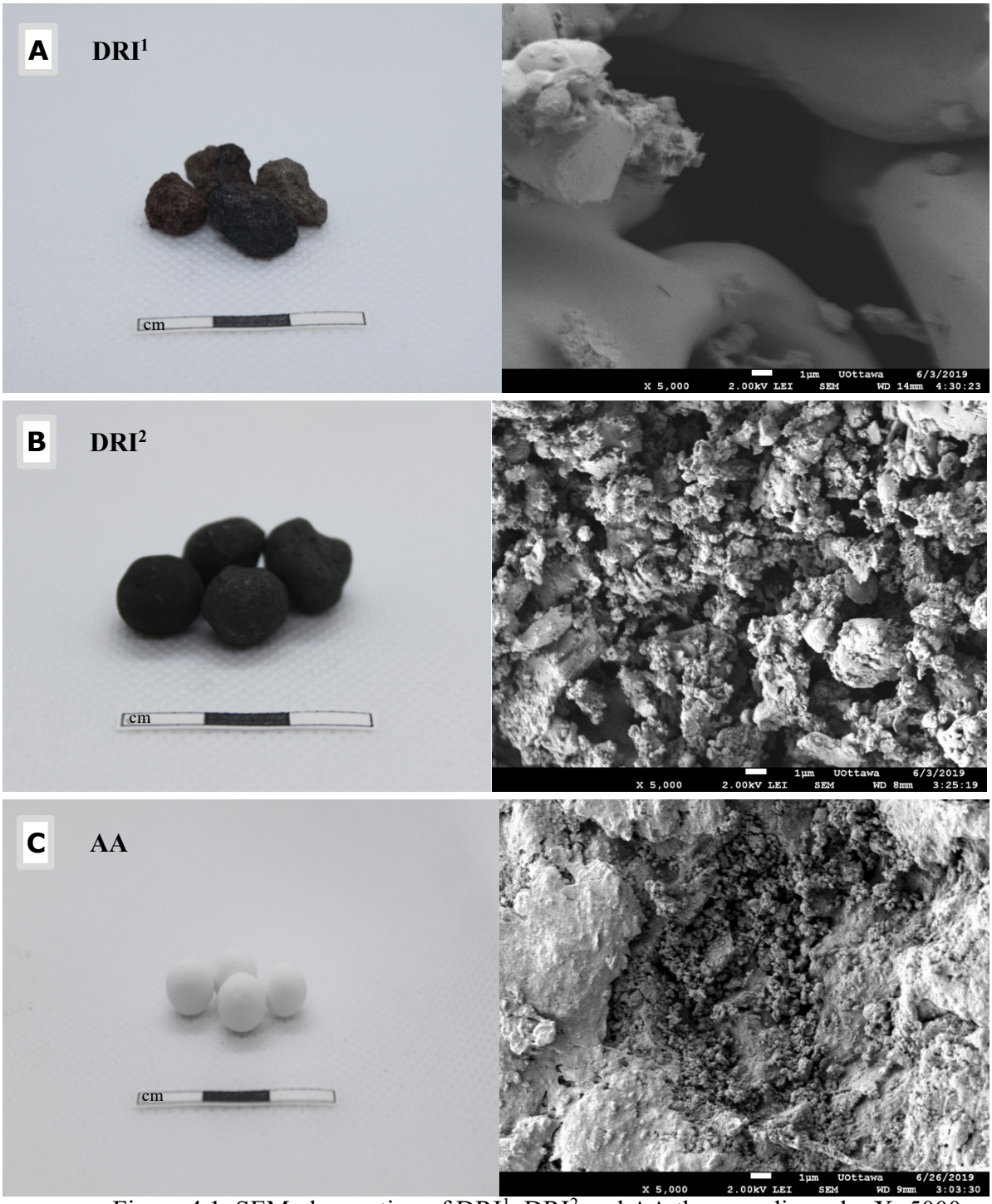


Figure 4.1. SEM observation of DRI[1], DRI[2] and AA three media under X=5000 magnification

4.5.2. PHOSPHORUS REMOVAL CAPACITY

In the preliminary batch trial, DRI^1, DRI^2 and AA jar tests were conducted with initial phosphorus concentration of 200 ppm. 10 grams media and 200 ml phosphorus solutions were shaken for 7 - 10 days to reach their adsorption equilibrium. At equilibrium state, only 4% of TP removed was found in the precipitate form therefore we assume that 100% of TP removed was via adsorption/accumulation onto the media surface. The maximum phosphorus removed was calculated and normalized as removal capacity per mass and bulk volume of media as presented in Table 4.7. Based on per gram media, AA achieved the highest removal capacity with 2.1 mg P/g by mass of the media, compared to 1.9 and 1.2 mg P/g for DRI^1 and DRI^2, respectively. However, based on per bulk volume of media, DRI^1 achieved the highest removal capacity of 2.6 kg P/m^3 with DRI^2 and AA removing 1.9 and 1.6 kg P/m^3, respectively. In order to compare capacity for filter media, volumetric capacity is more appropriate since it quantifies the performance of the same volume of filter.

Table 4.7. P removal capacity of three media under 200 ppm initial concentration

Media	DRI^1	DRI^2	AA
P removal capacity per mass media	1.92 ± 0.23 mg P/g	1.16 ± 0.39 mg P/g	2.14 ± 0.14 mg P/g
P removal capacity per bulk volume of media	2.6 ± 0.31 kg P/m^3	1.9 ± 0.64 kg P/m^3	1.6 ± 0.1 kg P/m^3

Based on the initial trial results, further batch studies were conducted using the DRI^1 media; although all three medias demonstrated high P sorption capacity and warrant further investigation. The impact of P concentration on sorption capacity was evaluated in

these batch trials. Media saturation was reached after 7 – 10 days in each test, with residual phosphorus concentrations decreasing to below the detection limit or reaching an equilibrium constant (showed in Appendix A). The maximum phosphorus retaining capacity in relation to phosphorus concentration was investigated using 10 g of DRI as exhibited in Figure 4.2. Each point represented the maximum P removal capacity and P concentration at the equilibrium state. The phosphorus removal capacity of the media increases with increasing P concentration, and appears to reach a plateau as initial P approaches 3000 mg/L. It appears that at initial P concentrations of less than 3000 mg/L, maximum phosphorus capacity is limited by the concentration. The Langmuir and the Freundlich isotherms were used to describe P removal capacity with equilibrium concentration in Figure 4.2.

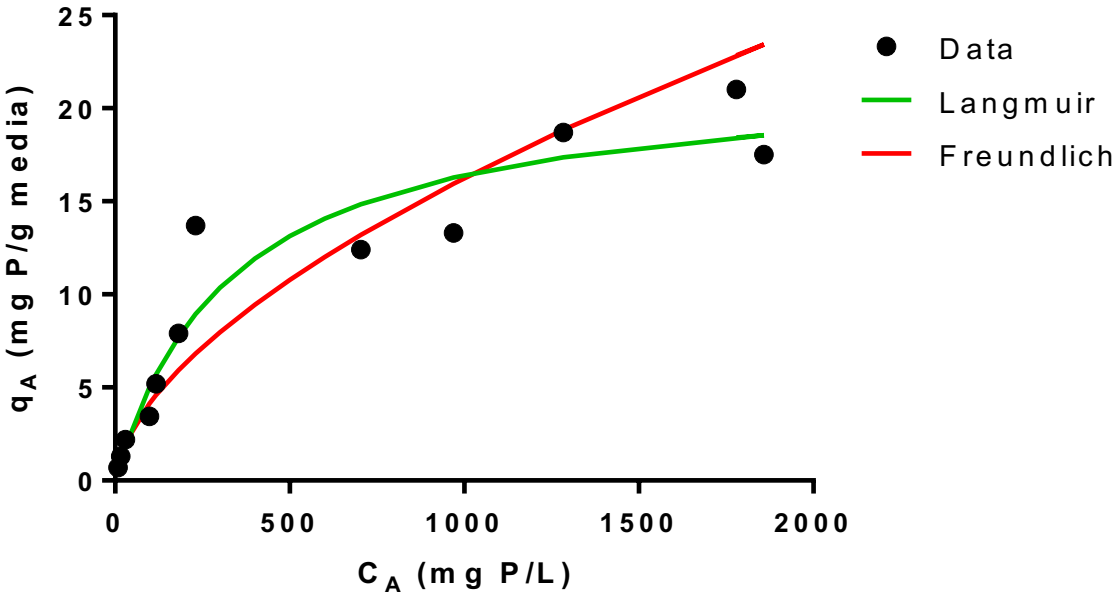
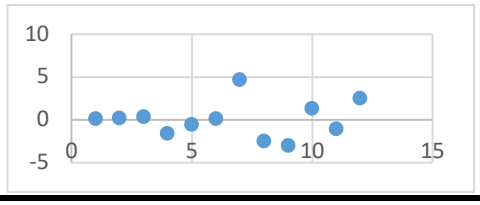
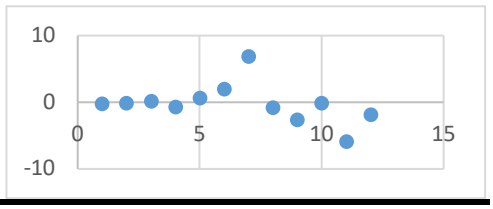


Figure 4.2. Phosphorus retaining capacity and P concentration under equilibrium state with the Langmuir and the Freundlich isotherms models

The coefficients of Langmuir and Freundlich models were obtained via interpreting data into linearized models and showed in Table 4.8. The R^2 of linearized Langmuir and Freundlich models were very close with 0.944 and 0.940 respectively. As well, the residual mean squares (MS) and plot of residual were evaluated to measure the quality of fit of the two models. The Langmuir model achieved a lower MS with 2.356 compared to the Freundlich model of 3.305, which indicates the Langmuir model provides a better fit to the data. By observing the plot of residuals, the randomness of residual of the Langmuir model is better than the Freundlich model. Over all, the Langmuir model can better describe phosphorus sorption by DRI media.

Table 4.8. Adsorption isotherms and quality of fit measuring parameters

	Langmuir	Freundlich
Model	$q_A = \frac{0.066C_A}{1 + 0.003C_A}$	$q_A = 0.274{C_A}^{0.591}$
R^2 (linear regression)	0.944	0.940
Residual mean squares (MS)	2.356	3.305
Plot of residual		

As of the time of writing, few studies on DRI as a phosphorus removal media have been found. Xue et al. (2018) investigated wastewater P removal with DRI media and the

saturated capacity of 3.25 mg P/g was found. Wang et al. (2015) discovered that microbial-collaborating DRI could reach over 90% of TP removal with an influent TP concentration of 8.08 mg P/L. However, results may be compared with studies investigating other "active" porous metallic media filters. Blast furnace (BOF) and electric arc furnace (EAF) slag are some of the most commonly studied "active" phosphorus filters. For BOF filters, P removal capacities (PRCs) of 0.1 – 0.58 mg/g media were observed (Baker et al., 1998; Drizo et al., 1999; Mann, 1997) with initial P concentration up to 100 mg P/L while with this P concentration, DRI media could reach a capacity of ~1.75 mg P/g. Other studies highlighted significantly higher PRCs, with a recent study on BOF-slag attaining 5.4 mg/g of media in batch assaying with 300 mg/L TP influent (Han et al., 2016). With the same concentration, DRI media was predicted to have the capacity of 4.33 mg P/g. EAF slag studies generally obtained slightly higher PRCs because the EAF slag contains higher iron content (Yildirim and Prezzi, 2011). Zeolites are aluminium-silicates having a porous structure consisting of silicon, aluminium and oxygen ions. Limestone, calcite, and dolomite are sedimentary rocks that are largely composed of calcium carbonate, whilst dolomite contains magnesium ($CaMg(CO_3)_2$). An alternative phosphorus retaining process receiving municipal water source by utilizing industrial by-products with high silica and calcium contents as a passive filter system has been studied in conjunction with a constructed wetland (Barca et al., 2014; Cameron et al., 2003; Hylander et al., 2006; Mortula et al., 2007). Such products include slags, shell sands, opoka and Polonite®. In one study, Polonite® achieved significant P retaining capacity as 1.3 mg P / g while slags, opoka and sands performance below 0.5 mg P / g in a study performed by Hylander et al. (2006). The adsorption capacities of minerals appear to be 0.1 mg/g, 0.45 mg/g and 0.6 mg/g for

zeolite, calcite and limestone respectively (Bjorn M. Sellner et al. 2019). Batch assay results are, however, somewhat difficult to compare due to the impact that assay parameters (i.e. influent P concentration, influent chemical characteristics, water and substrate ratio) have on the removal mechanisms. This issue has been raised numerous times by researchers investigating phosphorus absorbent materials (Cucarella and Renman, 2009).

It is hypothesized that there are two main potential mechanisms of phosphorus removal by DRI: 1) chemical adsorption and 2) surface precipitation and crystallization. During the adsorption process, dissolved P species $H_xPO_4^{(3-x)-}$ are transported into the porous DRI via diffusion and are then concentrated on the solid surface by chemical reaction (chemisorption), which is, in most of cases, limited by concentration (John C Crittenden et al., 2012). And crystallization could happen subsequently with the reduction of the solubility of the solute such as evaporation, cooling, addition of a second solvent and so on.

4.5.3. CRYSTAL FORMATION

The crystal/phosphate precipitation on the media surface was observed by SEM (scanning electron microscopy) analysis and the elemental composition of the crystal/surface precipitation was conducted by EDS (Energy Dispersive X-Ray Spectroscopy). There were two principal forms of crystal observed on the DRI surface as can be seen in (a) and (b). In (a), the crystal is clearly in plate form varying from 10 to 100 μm in length. The EDS analysis showed that the plate form crystal is composed of 80% Fe, 15% O, 4% P and 1% K by weight, which could be speculated to mainly consist as ferric oxide hydroxide based on stoichiometry. Similar plate crystals were found in the

precipitate, which was determined to be ferric oxide hydroxide ($Fe_2O_3 \cdot H_2O$) by PXRD analysis using a Rigaku Ultima IV diffractometer (Tokyo, Japan). In (b), the crystal is in the form of clustering sphere-like substance with sphere diameters of approximately 1 μm, which was also observed by Song et al., (2015) with sphere-like iron phosphorus crystal and ~1 μm diameter. The EDS results showed that the crystal was composed of 61% O, 14% P, 14 % Fe and 12% of K. Based on stoichiometric calculation, the main form is likely to be KFe $(PO_4)_2(H_xO_8)$. The KFe $(PO_4)_2(H_xO_8)$ crystal was found to be significantly dominant than other crystal species on the fully saturated DRI surface. From the SEM photos, it appears that surface precipitation/crystallization is dominant while adsorption may be involved at early stages. Li and Stanforth (2000) stated that it was difficult to distinguish chemical adsorption and surface precipitation even though the adsorption isotherm showed good fit. In this study it was believed that both mechanisms were involved in the P retaining process.

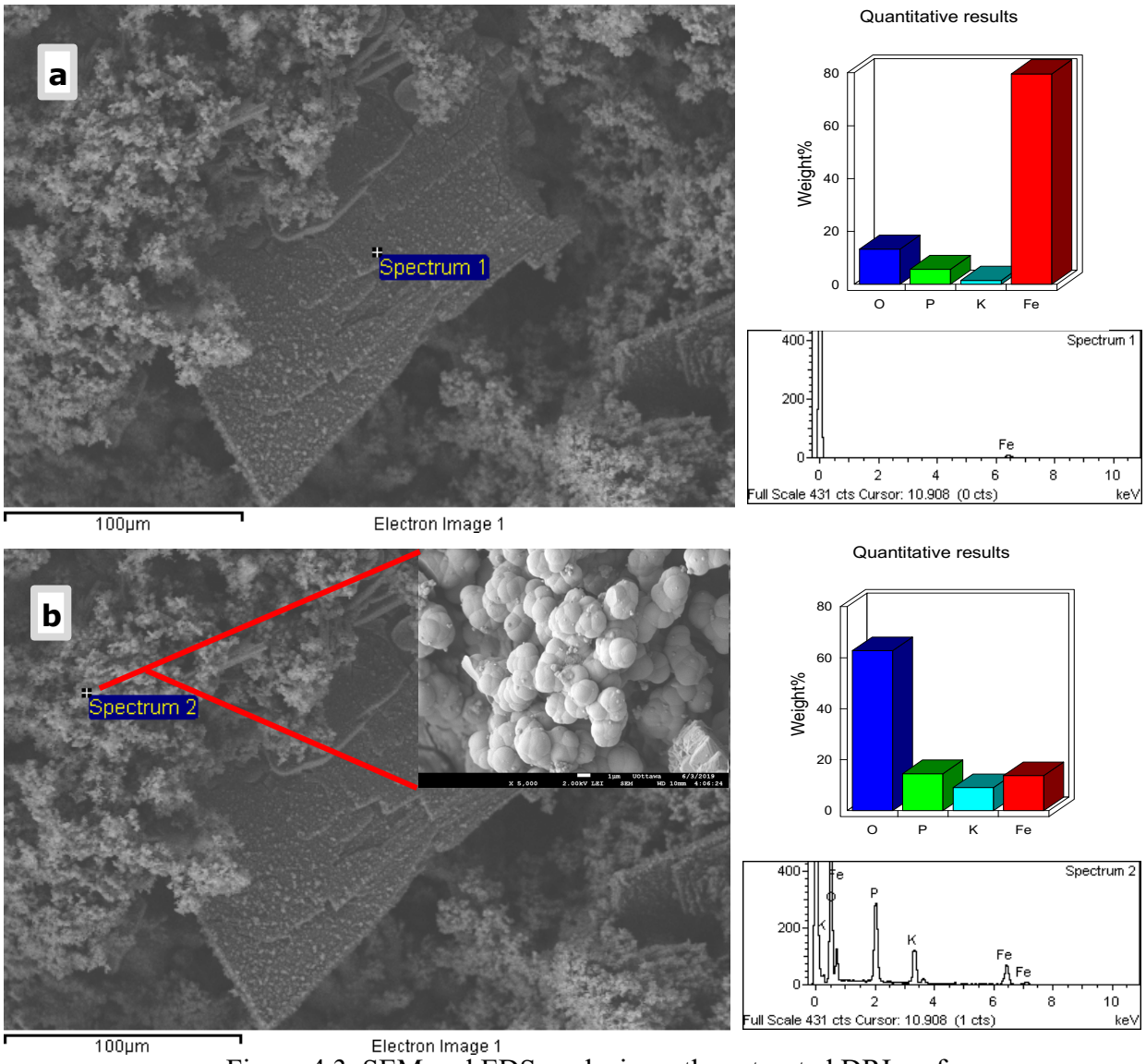


Figure 4.3. SEM and EDS analysis on the saturated DRI surface

After the batch test reached the equilibrium state, total iron and soluble iron concentration in the residual liquid were tested and found to be stable at 15.5 and 0.34 - 2.45 mg Fe/L, respectively. Most rivers contain concentrations of dissolved iron of 0.2-4 mg/L (Pokrovsky and Schott, 2002), and for some groundwater sources containing high soluble iron, iron concentrations were found to be 7-15 mg/L in Quebec, Canada (Ellis et al., 2000). Soluble iron is rarely found in concentrations greater than 10 mg/L in natural

waters (Ityel, 2011). Hence, the iron leaching potential is of minimal risk to the environment, particularly when considering any dilution effect in the discharging watershed.

During batch experiments, pH was observed to increase at pH 10.20-10.50. The reason that caused pH increase could be explained by electrochemical reaction on the surface of DRI. In the anode, element iron became Fe^{2+} and Fe^{3+} giving off electrons while in the cathode, O_2 and H_2O received electrons and formed OH^- (See Equation 4-6) and Equation 4-7).

$$Anode: Fe \rightarrow Fe^{2+} + 2e^- \rightarrow Fe^{3+} + 3e^- \qquad \text{Equation 4-6}$$

$$Cathode: O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \text{Equation 4-7}$$

4.5.4. MEDIA REJUVENATION AND PHOSPHORUS RECOVERY

Two strategies for media rejuvenation were initially investigated utilising two iron salts and two acid solutions at varying molarity and normality. The results presented in Figure 4.4 exhibit excellent regenerating capacities for all the solutions tested as well as moderate improvement with increasing molarity/normality: 93% to 95% from 0.023 M to 0.048 M Fe^{3+} ($FeCl_3$), 85% to 96% from 0.026 M to 0.052 M Fe^{3+} ($Fe_2(SO_4)_3$), 106% to 120% from 0.4 N to 0.8 N HCl and 121% with both 1.2 N and 2.2 N H_2SO_4.

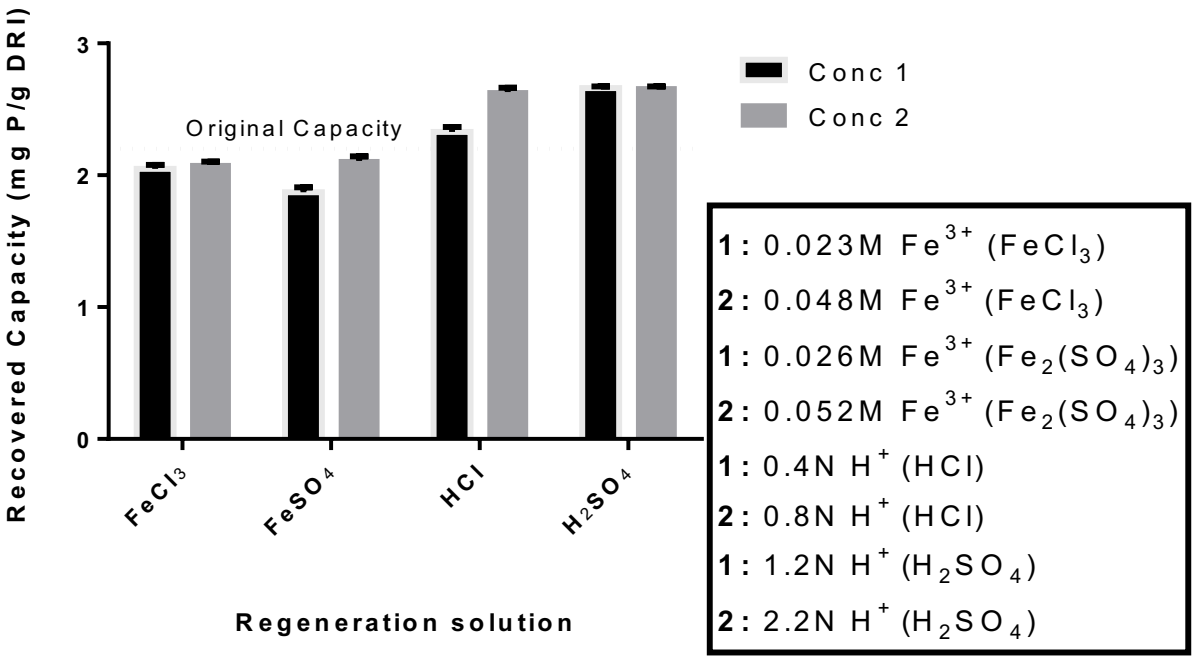


Figure 4.4. Regenerated phosphorus removal capacity under four regeneration solutions ($FeCl_3$, $Fe_2(SO_4)_3$, HCl and H_2SO_4) of two concentrations (1 and 2, which were listed on the figure) for 48 hours

Regeneration experiments were subsequently conducted with a series of lower concentrations of HCl and H_2SO_4 regeneration solutions at shorter retention times, to optimize regeneration practices with results presented in Figure 4.5. The results showed that even with a much lower concentration, the acids achieved decent capacity regeneration rate with 67% to 84% for HCl and 64% to 84% for H_2SO_4. The increase of concentration (0.05 N – 0.20 N) seemed had larger impact than the increase of regeneration time (3 h – 24 h). In 4.7 (a), HCl solutions regained 2.97% of original P removal capacity of DRI from 3 h to 24 h regeneration times while achieved 12.57% increase from 0.05 N to 0.20 N concentration. In 4.7(b), H_2SO_4 solutions recovered 9.98% of capacity from 3 h to 24 h regeneration times with 11.16% recovery rate from 0.05 N to 0.20 N.

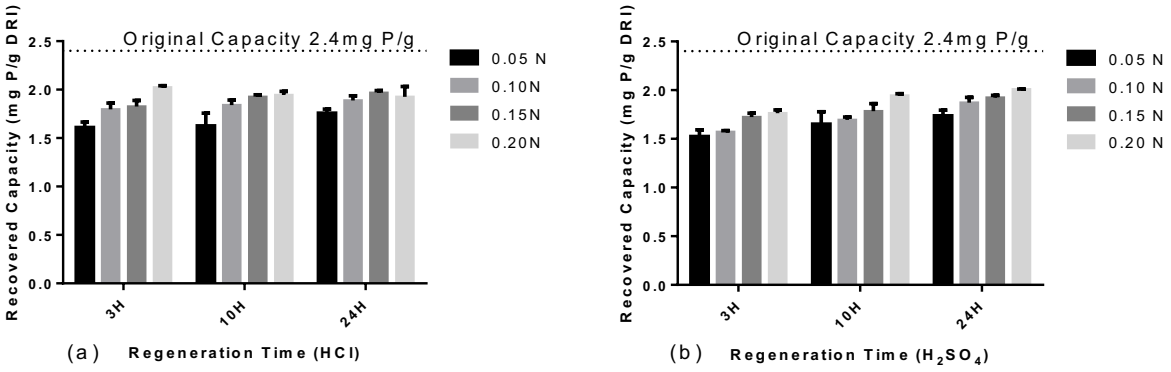


Figure 4.5. DRI regenerated by HCl and H_2SO_4 under 4 concentrations and 3 regeneration times

The total phosphorus in the spent regeneration solutions was tested and results are shown below in Figure 4.6. $FeCl_3$ and $Fe_2(SO_4)_3$ solutions did not recover any significant quantities of phosphorus (< 0.02 and 0.42% respectively), whereas HCl and H_2SO_4 both achieved a higher TP recovery rate at 180 min with 11.4% and 37.6% of TP recovery rate for 0.40 N HCl and 1.2 N H_2SO_4, respectively. It appears that the increase of the presence of H^+ and the three hours regeneration time favours the TP recovery.

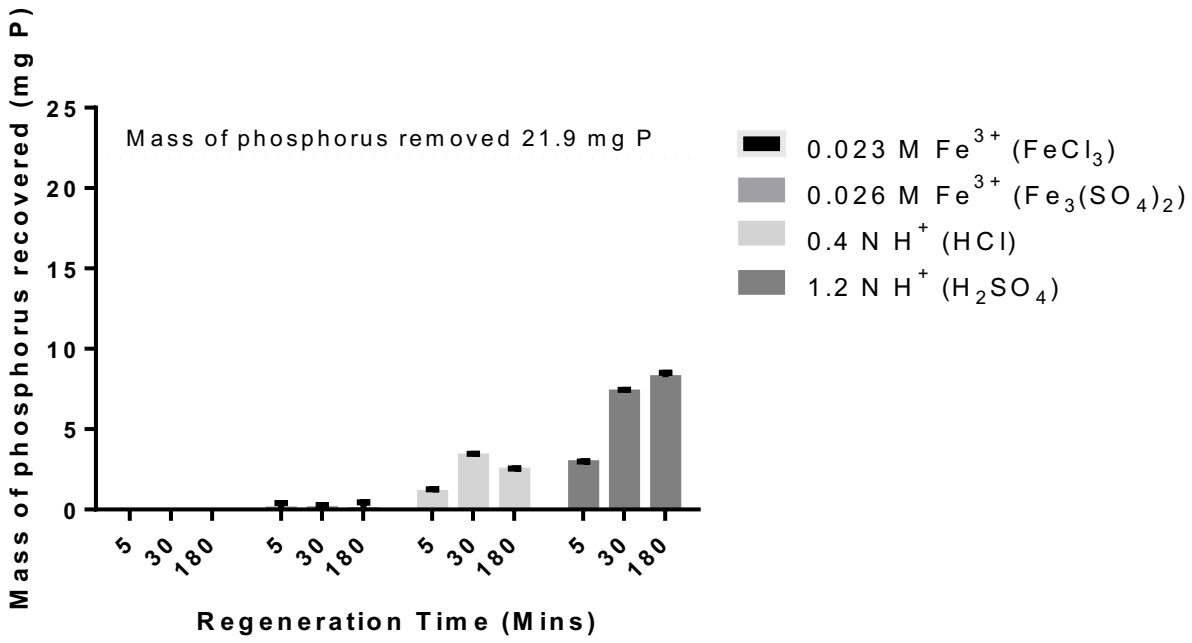


Figure 4.6. Phosphorus recovery of the four regeneration reagents with three regeneration times

To investigate how a lower concentration of regeneration solution impacts the extent of phosphorus recovery, ortho-phosphorus and total phosphorus in the spent regeneration solutions of HCl and H_2SO_4 were analyzed and graphed in Figure 4.7. It showed that the recovered phosphorus was in both soluble and insoluble forms and the recovered particulate phosphorus accounted for about 77% of the total phosphorus recovered.

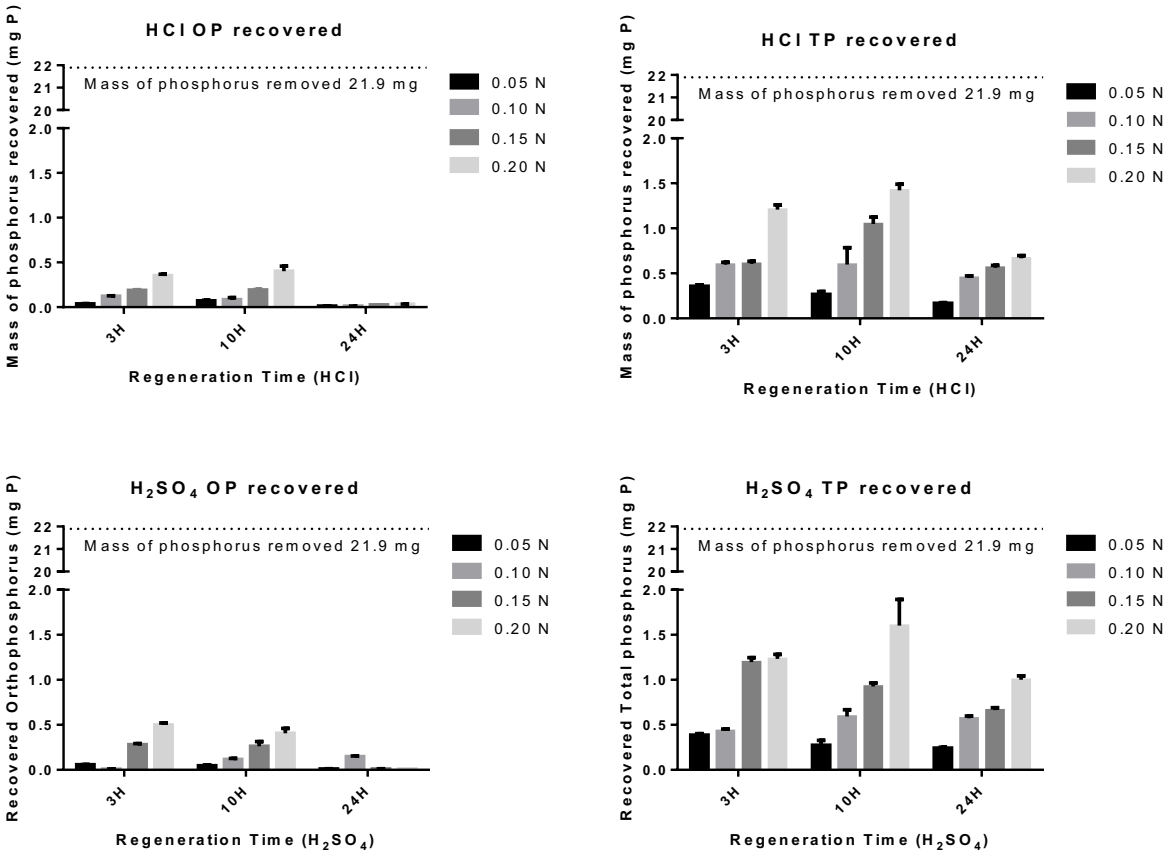


Figure 4.7. Ortho-phosphate (OP) and total phosphorus (TP) recovery rate under HCl and H_2SO_4 chemical treatment with 3, 10 and 24 hours treatment time and acid concentrations 0.05, 0.10, 0.15 and 0.20 N

The optimum regeneration time was found to be 3 hours for 0.05 – 0.20 N HCl and H_2SO_4, with 1.63 – 5.52% and 1.77 – 5.63% TP recovered, respectively. A higher regeneration time of 10 / 24 h achieved a lower P recovery rate, which could be explained by P re-sorbing/crystallizing on the regenerated DRI media. Regardless, the phosphorus recovery rate is still low in the low concentration regeneration solution. In order to increase P recovery rate, the concentration of the regeneration solution needs to be increased. Although the P recovery rate is low using 0.05 – 0.2 N acid as H^+, over 80% of the DRI media capacity recovery was achieved. Therefore, the balance from the economical point

of view and the pursuit of high P recovery rate should be considered when determining the concentration of regeneration solution.

In order to increase the phosphorus recovery rate, increasing the regeneration solution concentration could lead to much higher recoveries, due to a shifting of the chemical equilibrium. Meanwhile, the regeneration time did not appear to have a major impact on either P recovery or regenerated capacity of the spent DRI. On the other hand, longer regeneration times have the potential for causing of P to re-sorb/crystallize on the DRI media. The concentration of 0.05–0.8 N HCl regenerated 67–120% of the original DRI capacity, and H_2SO_4 achieved similar results with 64–121% capacity recovery rate under 0.05 – 2.2 N concentrations. Saturated media treatment with both HCl and H_2SO_4 were able to increase P removal capacity above initial values. This is likely due to etching of the DRI's surface which liberated additional adsorption sites as well as by removing iron oxides from the media surface. The acid treatment could also potentially improve the interconnectivity of the DRI's internal pore structure, effectively increasing the specific surface area of the media.

The phosphorus retention capacity of DRI can be fully regenerated by simple chemical treatment. Low concentration solutions of 4 types of regeneration reagents (HCl, H_2SO_4, $FeCl_3$, and $Fe_2(SO_4)_3$) were investigated in this study. All reagents were capable of regenerating the DRI's P removal capacity, with a maximum of 95% of the capacity being recovered after exposition to 0.048M Fe^{3+} ($FeCl_3$), 96% after exposition to 0.052M Fe^{3+} ($Fe_2(SO_4)_3$), 120% after exposition to 0.8 N H^+ (HCl) and 121% after exposition to 2.2 N H^+ (H_2SO_4). 0.4 N H^+ (HCl) and 1.2 N H^+ (H_2SO_4) recovered a maximum of 11.4% and 37.6% of phosphorus from the media, respectively, while $FeCl_3$ and $Fe_2(SO_4)_3$ did not

demonstrate any significant potential of P recovery. Hence, the media could be used for multiple cycles before fully losing its functionality and the reuse of regeneration solutions should be considered.

4.6. CONCLUSIONS AND RECOMMENDATIONS

Preliminary investigations of DRI have demonstrated that it is a suitable media to remove phosphorus from stormwater and wastewater sources. The unique features of DRI compared to other phosphorus retaining filter media include a high content of metallic iron and a highly porous internal and external structure allowing for a relatively high phosphorus retaining capacity, which was well described by the Langmuir adsorption isotherm. By reviewing literature, common phosphorus retaining adsorbents such as limestone, calcite, and dolomite, slags, shell sands, opoka and Polonite® generally have lower P removal capacity compared to DRI. Chemical adsorption and crystallization are believed to be the major P removal mechanisms with ferric phosphate crystal growth observed under SEM/EDS. Residual total iron concentrations were found to be within concentration ranges commonly found in natural waters. Media regeneration studies demonstrated that both Fe^{3+} and H^{+} solutions can effectively restore P removal capacity from saturated media, while only H^{+} solutions were also capable of recovering P from the media. Increasing regeneration solution concentration increased media capacity while increasing regeneration time could favour re-sorption/surface crystal growth. A generation solution concentration 0.05 M Fe^{3+} or 0.4 N H^{+} could achieve 100% P removal capacity regeneration. A maximum of 37.6% P was recovered under a concentration of 1.2 N H^{+} solution, suggesting higher H^{+} could increase P recovery.

It is recommended that column/pilot research be conducted on DRI to determine removal loading rate, hydraulic retention time and lifespan, as these will be important design factors for phosphorus reduction applications in the future.

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CHAPTER 5 : THE FACTORS THAT AFFECT DIRECT-REDUCED IRON (DRI) COLUMN ON THE PHOSPHORUS REDUCTION EFFICIENCY

5.1. SETTING THE CONTEXT

The manuscript presented in Chapter 5 is titled *The factors that affect direct-reduced iron (DRI) column on the phosphorus reduction efficiency* by H. Qin, C. Kinsley, and P. M. D'Aoust. This article firstly introduced direct-reduced-iron (DRI) in terms of its density, specific surface area, morphology and elemental composition. Secondly, this article investigated P removal in column studies by using synthetic P solutions and augmented real municipal facultative wastewater lagoon effluent in a continuous upwards flow configuration. The column study investigated the impact of hydraulic retention time, phosphorus loading rate, DRI filter media nominal diameter, DRI media/gravel mixture and temperature on phosphorus removal performance. Finally, the article attempts to predict the media's life span and design parameters for typical wastewater treatment applications.

5.2. ABSTRACT

Phosphorus is a biologically active compound which has been intensely extracted and utilized by humans to enhance agricultural productivity. However, when allowed to enter natural aquatic environments in excess quantity, it can have deleterious effects on water quality and human health. This study evaluated the performance of two novel phosphorus removal filter media: direct-reduced iron (DRI) and activated alumina (AA). These materials were investigated in laboratory scale column studies to evaluate their efficiency in terms of capturing and retaining phosphorus from synthetic and real wastewaters. Three sizes of DRI media (3.5 mm,11 mm and 12.5 mm) and one size of AA media (7.5 mm) were investigated under synthetic P solutions from 2 to 10 mg/L over a period of 315 days while varying HRT from 0.7 to 15 h (average HRT). The columns were capable of removing > 80% of the influent phosphorus with HRTs ranging from ~5 to 15 h HRT (except 19 mm DRI media) as media size and P concentration increased. Columns containing similar-sized DRI[1] (11 mm), DRI[2] (12.5 mm) and AA (7.5 mm) in 1-1 mixture with pea stone (10 mm) were also investigated using municipal lagoon effluent augmented to 4 mg P/L while varying HRT from 0.7 – 5 h and temperatures of 25ºC and 4ºC. The media were observed to perform closely to synthetic solution columns and the media filling percentage did not significantly affect the removal efficiency under the same HRTs. Minimum P retaining capacities of the four media after 1 year of continuous column loading were: 2.18, 1.82, 1.22 and 3.13 mg P/g media for 3.5 mm, 11 mm, 19 mm DRI[1] and 7.5 mm AA media, respectively. The two major mechanisms of P removal are hypothesised to be adsorption and crystal precipitation. Filter sizing to treat 80% P per m^3/d for stormwater, municipal lagoon effluent, septic system effluent and dairy wastewater

were estimated to be 0.24, 4.69, 15.3 and 36.2 m^3 with 10 years lifespan. The results of this study lay the groundwork for future field-scale study of DRI as a new phosphorus-removing media.

5.3. INTRODUCTION

Phosphorus (P) is frequently a limiting nutrient for plant, algae, macrophyte and microorganism growth in aquatic environments. In water and wastewater, the most commonly encountered form of P is orthophosphate (PO_4^{3-}-P), causing it to be the most commonly targeted P-containing compound for removal (Carpenter, 1985). North American waters are highly impacted by nutrients, with studies suggesting that up to 50% of lakes and 60% of rivers are affected by an excess in nutrient input. This has led to eutrophication becoming a topic of great concern for many in the United States and Canada (Beauchemin and Simard, 2011; Parry, 1998; USEPA, 2002). The agricultural industry is unequivocally one of the largest contributors to nutrient pollution in surface waters globally. It is estimated that internationally, the livestock industry alone was responsible for contributing to between 14 – 72% and 32 – 94% of the nitrogen (N) and P entering the natural environment, respectively (FAO and LEAD, 2006). Other sources of phosphorus impacting surface waters include: industrial effluents, urban stormwater, centralized and decentralized domestic wastewater treatment systems. Chemical precipitation of P in wastewater with metal salts remains the preferred method due to its effectiveness (Jiang and Graham, 1998), however, the operation of coagulation and sludge management systems is impractical for diffuse sources of pollution such as agricultural drainage or stormwater runoff. In these cases, as well as with low-flow decentralized wastewater applications, reactive filter-type removal systems may be preferable and/or more cost effective. Filter-type facilities utilizing iron or metal-rich aggregate or media such as slag (Claveau-Mallet et al., 2012; Okochi and McMartin, 2011), natural minerals (Bellier et al., 2006; Gustafsson et al., 2008) or zeolites (Xie et al., 2015) have demonstrated success in

capturing and retaining phosphorus. In this paper, the P-retention efficiency and P retaining capacity of a novel, previously untested iron-rich media, direct-reduced-iron (DRI), was studied in the upwards flow column configuration. DRI is an intermediate product in the steel industry, produced from iron ore in direct-reduction steel plants, and is a moderately porous, iron-rich aggregate.

5.4. MATERIALS AND METHODS

5.4.1. FILTER MEDIA

In this study, three types of media: DRI[1], DRI[2] and AA were investigated as the filter media of fixed-bed columns. DRI[1] (average diameter 3.5 mm, 11 mm and 19 mm) and AA (7.5 mm) were acquired from Gongyi City Meiqi Industry Co., Ltd's reduction plant (Gongyi City, Henan Province, China). DRI[2] was acquired from ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada with an average 12.5 mm diameter. Pea stone (10 mm) was used as non-reactive media to form 50% (%v/v) pea-stone/DRI blends which was acquired from King Packaged Materials Company (Oakville, Ontario, Canada). The detailed information of three medias were shown in the below Table 5.1.

Table 5.1. Media dimension and location of origin

Media	DRI[1]	DRI[2]	AA	Pea stone
Diameter	3.5, 11, 19 mm	12.5 mm	7.5 mm	10 mm
Location of origin	Gongyi City Meiqi Industry Co., Ltd's reduction plant (Gongyi City, Henan Province, PRC)	ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada	Gongyi City Meiqi Industry Co., Ltd's reduction plant (Gongyi City, Henan Province, PRC)	King Packaged Materials Company (Oakville, Ontario, Canada)

5.4.2. MEDIA CHARACTERIZATION

Three medias were characterized in terms of density, surface morphology and chemical composition. Specific gravity was determined as per ASTM C127– 07. The specific surface area was determined via Brunauer-Emmett-Teller (BET) analysis utilizing a TriStar 3000 (Micromeritics Instrument Corp, Norcross, GA, USA) at McGill University's Materials Characterization laboratory (Montreal, QC, Canada).

Morphological and chemical information on the DRI media was obtained via Energy Dispersive X-ray Spectroscopy (EDS) coupled with Scanning Electron Microscope (SEM) imaging, utilizing a JSM-7500F FESEM microscope at the Centre for Catalysis Research and Innovation (CCRI) at the University of Ottawa (Ottawa, Ontario, Canada). Finally, information on the complete chemical composition of the DRI was determined via ICP-OES utilizing a 5110 SVDV (Agilent, United States) at the University of Ottawa's Advanced Research Complex.

5.4.3. FIXED-BED COLUMN STUDY

Laboratory-scale upwards-flow column experiments were performed to quantify the influence of the filter media's nominal diameter, column hydraulic retention time, water chemical characteristics, media pairing practices and temperature on phosphorus removal performance. Upwards flow configuration was used to reduce hydraulic circuiting under the influence of gravity.

Synthetic wastewater columns: DRI[1] with nominal diameters of 3.5 mm, 11 mm and 19 mm and AA with an average diameter of 7.5 mm were utilized in four identical cylindrical columns measuring 100 dia. x 317.5 mm with top outlet A and middle outlet B (see Figure 5.1). Synthetic influent solutions with concentrations ranging from 2.0 – 10 mg P/L were dosed to the columns utilizing a peristaltic pump at different flowrates, to achieve average hydraulic retention times (HRT) varying from 0.7 to 15 hrs. These column tests were performed continuously over a period of 315 days, divided in seventeen distinct phases, with gradually increasing P loading rates (2 - 10 mg P/L and 2 - 43.2 L/d). Samples were collected and tested every 1 to 4 days, with more frequent testing at higher flowrates. Triplicate samples were collected once a week.

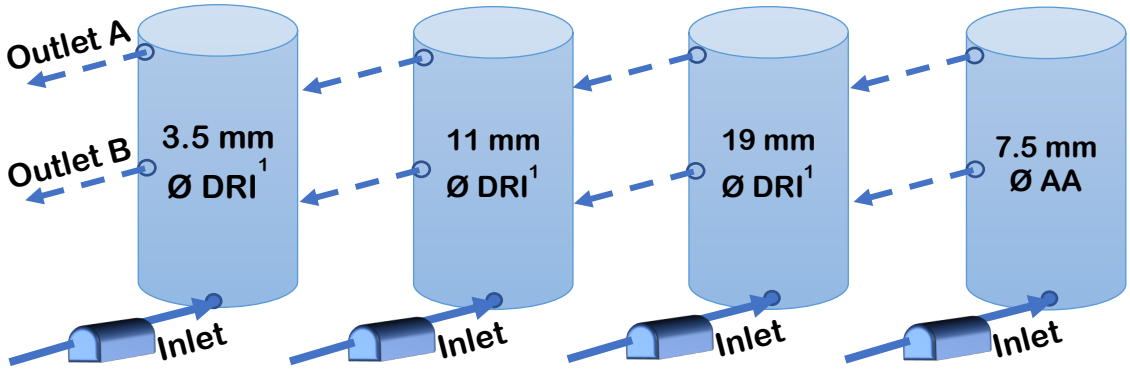

Figure 5.1. Fixed-bed column study utilizing synthetic phosphorus wastewater

Lagoon effluent columns: Raw wastewater was collected from the municipality of Casselman's municipal waste stabilization pond outlet located in Casselman, ON, Canada (Google Maps Plus Code: *8WF9+MV Casselman, The Nation Municipality, ON*) as the influent of four upflow columns. The cylindrical columns had the same dimensions as the previous experiment. DRI[1] (11 mm), DRI[2] (12.5 mm) and AA (7.5 mm) were mixed with pea stone to a 1:1 v/v ratio. A fourth column contained only pea stone was used as a blank reference column (as shown in Figure 5.2, below). The lagoon influent concentration was augmented to 4 mg/L-P as required, and pumped through the columns utilizing a peristaltic pump at different flowrates (6 - 43.2 L/d), to achieve average hydraulic retention times (HRT) of 0.7 - 5.0 hrs. Samples were collected up to 3 times a day for the first 3 days, and then once a day for the remainder of the experiment. Triplicate samples were collected once a week.

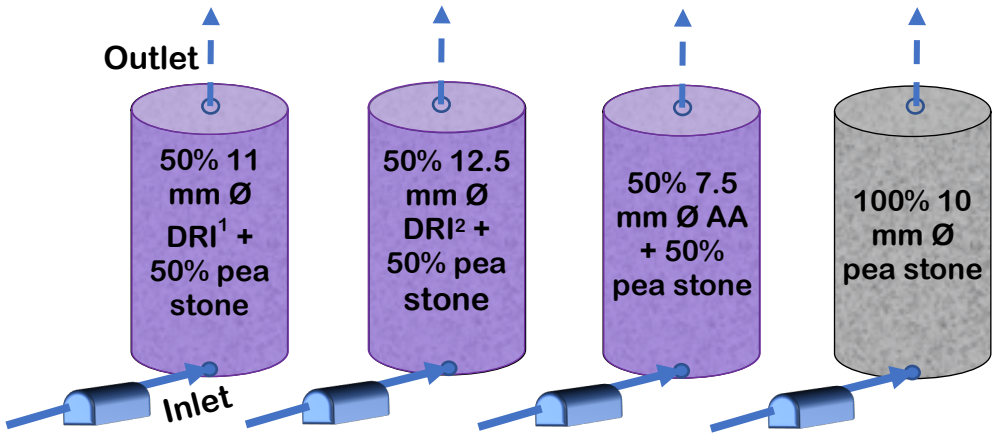

Figure 5.2: Fixed-bed column study utilizing P-augmented municipal lagoon effluent

5.4.4. WATER QUALITY ANALYTICAL METHODS

Total phosphorus and orthophosphates were measured as per SM 4500 P-D (APHA, WEF, 2012) (stannous chloride) under wavelength 690 μm, using a HACH DR6000 UV-VIS spectrophotometer (Loveland, CO, USA) coupled to a 50 mm quartz cuvette.

The pH measurements were performed using a HACH HQ40D handheld meter coupled to a PHC101 pH probe (Loveland, CO, USA).

Soluble and total iron concentrations were measured as per EPA Method 7000B (USEPA, 2007) using a PerkinElmer PinAAcle 500 Flame Atomic Absorption Spectrometer (Waltham, MA, USA).

In order to verify calculated HRTs in the column experiments, potassium bromide was utilized as a salt tracer to examine the hydraulic conditions existing within the reactors. Conductivity measurements were performed using a VWR sympHony B40PCID conductivity meter (Radnor, United States) with a VWR conductivity probe (Radnor, PA, USA). The results are presented in Appendix B.

5.5. RESULTS AND DISCUSSION

5.5.1. COLUMN MEDIA

The reactive media characteristics are presented in Table 5.2.

Table 5.2. Properties of the column media

Material	Diameter (mm)	STD (mm)	Density (g/cm^3)	Specific area (m^2/g)	Elemental content (%)	Bed density (kg/m^3)	Bed porosity (%)	Location of Origin
DRI[1]	3.5	0.70	3.22	0.33	87.5 (Fe)	1284	66	Gongyi City, Henan Province, PRC
	11	2.03				1357	52	
	19	5.85				1671	46	
DRI[2]	12.5	1.24	2.93	0.27	92.2 (Fe)	1653	41	Contrecoeur, Quebec, Canada
AA	7.5	0.32	1.34	250.2	100 (A_2O_3)	739	45	Gongyi City, Henan Province, PRC
Pea stone	10	1.13	2.62	n/a	n/a	1455	45	Oakville, Ontario, Canada

DRI – direct-reduced iron; AA – activated alumina

DRI[1] – acquired from Gongyi City Meiqi Industry Co., Ltd in Gongyi City, Henan Province, PRC.

DRI[2] – acquired from ArcelorMittal's direct reduction plant in Contrecoeur, Québec, Canada.

Water temperature 23ºC

Direct-reduced iron (DRI) is the main P-retention media of interest of this research project. DRI is an intermediate of the steel making industry that is manufactured by applying reducing gas (i.e. carbon monoxide) or coal to remove impurities such as oxygen, silicon, sulfide from the iron ore without melting the iron. Thus, the iron content of DRI is fairly high at approximately 85% (Anameric & Kawatra, 2007). In this study, DRI[1] was analyzed through ICP-OES having iron content of 87.5% and the iron composition of DRI[2]

is 92.2% which was provided by the manufacturer ArcelorMittal. Without melting, oxygen was extracted by reducing gas or coal to form carbon dioxide and escaped from the media leaving porous surface structure. DRI has surface area 0.27 – 0.33 m^2/g based on BET test, which is lower than the study of Anameric & Kawatra (2007) with an average surface area 0.5 - 4.0 m^2/g. Due to its high porosity, DRI has a relatively low density (2.93 – 3.22 g/cm^3) compared to conventional iron (7.87 g/cm^3) (Elert, 2007). This density is lower than traditional values for DRI produced via the MIDREX® process (3.40 – 3.60 g/cm^3) (Midrex, 2015), but is similar with findings of other studies on DRI (1.5 – 4.0 g/cm^3, 2.93 g/m^3) (AbdElmomen, 2013; Anameric and Kawatra, 2007).

Many other P-retaining media are functional due to the presence of Ca or Al, such as blast furnace slag, which is a waste material from the conventional blast furnace steel making process and is formed by limestone addition. The calcium-based media is highly pH dependent and performs in high pH condition (10 – 12) (Claveau-Mallet et al., 2012; Cucarella and Renman, 2009). Because of its low calcium content, the solution's pH has little increase in the column experiment with the hydraulic retention time below 24 hours with an average influent pH 6.8 and an average effluent pH 7.28.

Activated alumina is known for its high specific surface area which can reach over 200 m^2/g (Jovanović et al., 1992). The activated alumina was analysed to have 250.2 m^2/g specific surface area, highlighting its extremely dense porosity. Activated alumina is constituted by 100% Al_2O_3 which is chemically inactive.

5.5.2. COLUMN STUDY

Synthetic solution

A 315-day long packed media laboratory-scale column study of DRI[1] with three nominal diameters (3.5, 11 and 19 mm) and 7.5 mm activated alumina (AA) was conducted with synthetic phosphorus solutions. The loading rate was increased over time from influent concentrations of 2 to 10 mg/L while flowrate for each influent concentration was varied from 2 - 43.2 L/d, decreasing the average hydraulic retention time from 15 h to 0.7 h. The column study data is presented in Figure 5.3 with the data divided into 5 conditions based on initial P concentrations (C_0) from 2 – 10 mg P/L. In each phase, effluent concentration reached a steady state and column saturation did not occur during the 315 days study.

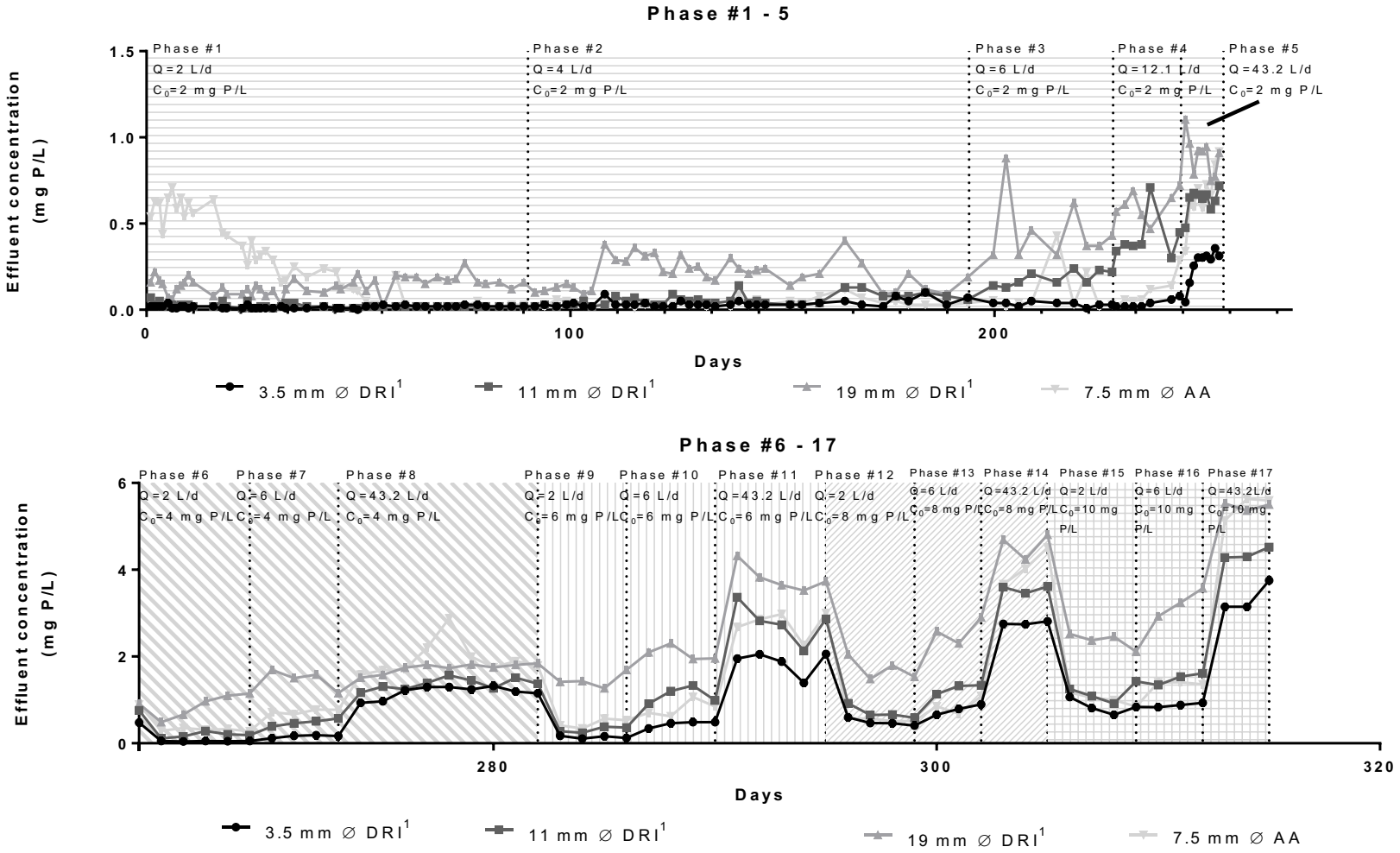

Figure 5.3. Effluent concentration of synthetic water columns for 315 days; phases were regrouped as five segments based on same C_0 (segment 1: phase #1-5; segment 2: phase #6-8; segment 3: phase #9-11; segment 4: phase #12-14; segment 5: phase #15-17); in each segment, flowrate was increased from 2 to 43.2 L/d

From Figure 5.3, it can be observed that for each influent concentration condition, effluent concentration (C_e) increased as flowrate increased. It can also be observed that C_e also increased as influent concentration (C_o) increased. In the comparison of different media, it was observed that smaller size media overall had lower effluent phosphorus while the large size media tended to have the highest C_e, indicating that larger contact area promoted higher removal. Activated alumina had low effluent P concentration during the first segment which was similar to small size DRI[1] (3.5 mm). From segment 2 to segment 5, AA performed similarly to 11 mm DRI[1] media.

The steady state removal efficiencies of 17 phases and four medias were summarized in Figure 5.4 with respect to influent concentration and HRT. The y-axis represented phosphorus removal efficiency (%) in four gradients, with blue in 80 – 100% range, yellow between 60% and 80%, gray in 40 to 60% and red under 40%.

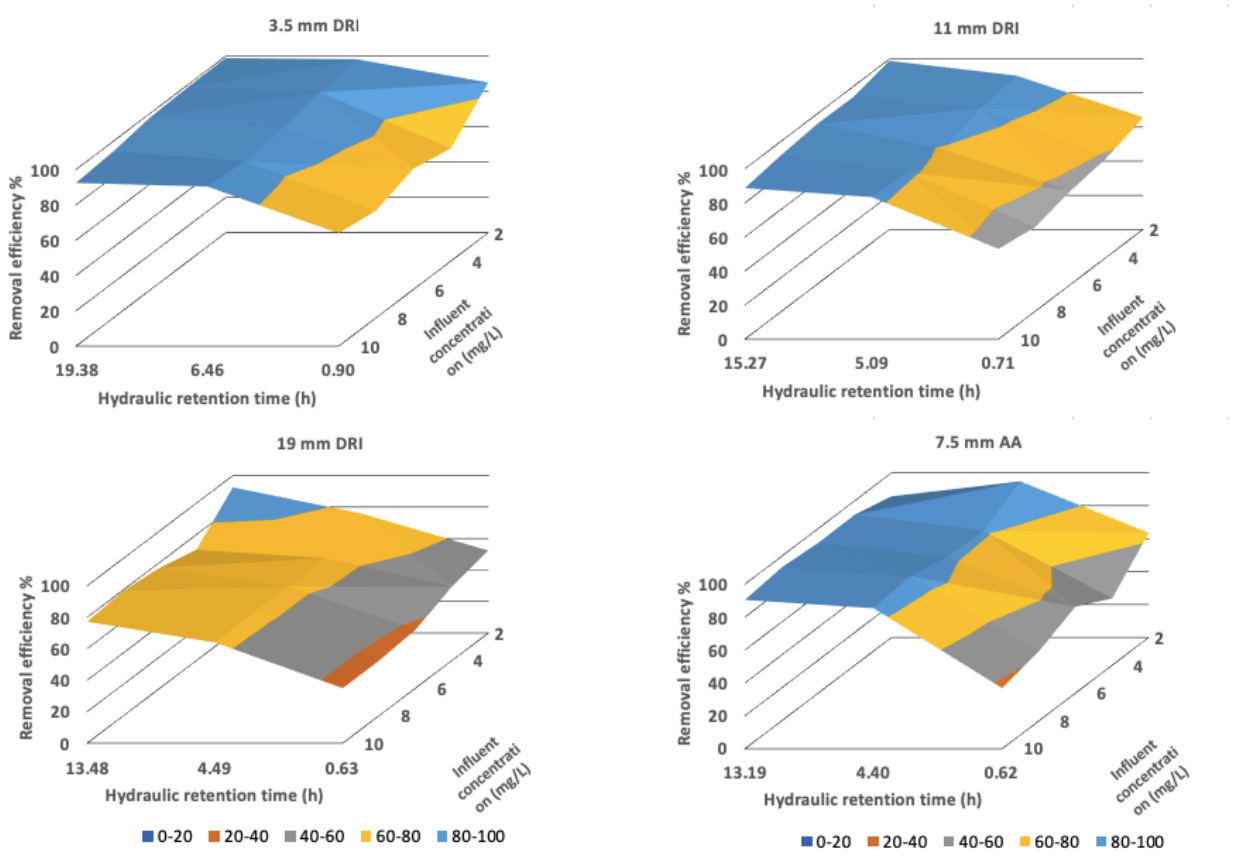

Figure 5.4. Removal efficiency of four media throughout 17 phases (steady state) (Blue: 80 – 100%; yellow: 60 – 80%; gray: 40 – 60%; red: below 40%)

The synthetic column study confirmed that the DRI was capable of maintaining P removal efficiencies 40% to 99% across a range of influent concentrations and HRTs, with average HRT varying from 0.7-15 h and influent concentrations C_0 varying from 2-10 mg P/L. Small media (3.5 mm) DRI[1] achieved the highest general removal rate, in which the removal efficiency dropped from 99% to 61% with increasing hydraulic and mass loading rates. In order to maintain an 80% removal rate, the minimum HRT required ranged from 0.9 – 4.4 h for 2 – 10 mg P/L C_0, respectively. The medium size (11 mm) DRI[1] removal efficiencies declined from 99% – 50%, and required 3.3 – 5.1 h minimum HRT to maintain 80% removal. The large size media removal efficiencies declined from 93-35% and required 6.3 – 13.5 h minimum HRT to maintain 80% removal for 2 – 10 mg P/L C_0,

respectively. The AA had removal efficiencies declining from 95 to 37% and required 2.7 – 3.9 h minimum HRT to maintain 80% removal for 2 – 10 mg P/L C_0, respectively. It can be seen that the hydraulic retention times required for 80% P removal are relatively low: ≤ 5 h for 3.5 mm, 11 mm DRI[1] and 7.5 mm AA while 15 h and beyond for 19 mm DRI[1]. These HRTs are lower than full/pilot scale phosphorus retaining filter wastewater treatment application, which typically use 2 – 7 days of hydraulic retention time was easily used (Barca et al., 2014; Park, 2009; Tanner et al., 1995).

In the column study, smaller sized media with higher porosity exhibited higher removal rates due to relatively larger surface areas to contact with the phosphorus. Influent concentration and hydraulic retention time were both shown to impact removal efficiency. Reduced contact time reduces time for diffusion of phosphorus to both the media surface and within the media pores, leading to lower removal efficiency. It is observed that the media size, influent concentration and HRT are the variables which control removal efficiency. In order to achieve a minimum of 80% removal for influent concentrations between 2 – 10 mg P/L, maximum hydraulic loading rates of 6, 2.5, < 0.82, and 3 $m^3/m^3/d$ HRTs for small, medium, large size DRI[1] and 7.5 mm AA, respectively. The outlet B effluent phosphorus concentration was analysed during six operating conditions, with results filling in the data displayed in Figure 5.4. The comparison of outlet A and B effluent P concentration is presented in Appendix C.

The influent loading rate versus average removal rate for each condition of the synthetic wastewater column study was plotted in Figure 5.5. The removal efficiency gradually reduced from 99% removal efficiency to 35% as the loading rate increased from 1.5 to 166 g $P/m^3 \cdot d$. The Figure demonstrates that small 3.5 mm DRI media achieved on

average a 12% higher removal loading rate than medium size DRI[1] and 28% higher than large sized 19 mm DRI. Activated alumina performed between medium and large DRI1. Small (3.5 mm) DRI1 maintained an almost 100% removal rate at influent loading rates below 9.9 g P/m3d and maintained > 80% removal rates below influent loading rate 33 g P/m^{3}d. For the 11 mm, 19 mm DRI1 and 7.5 mm AA, respectively, maximum loading rates of 23.2, 1.5 and 23.2 g P/m^{3}d can be applied to maintain > 80% removal rates, which could be considered as a design threshold.

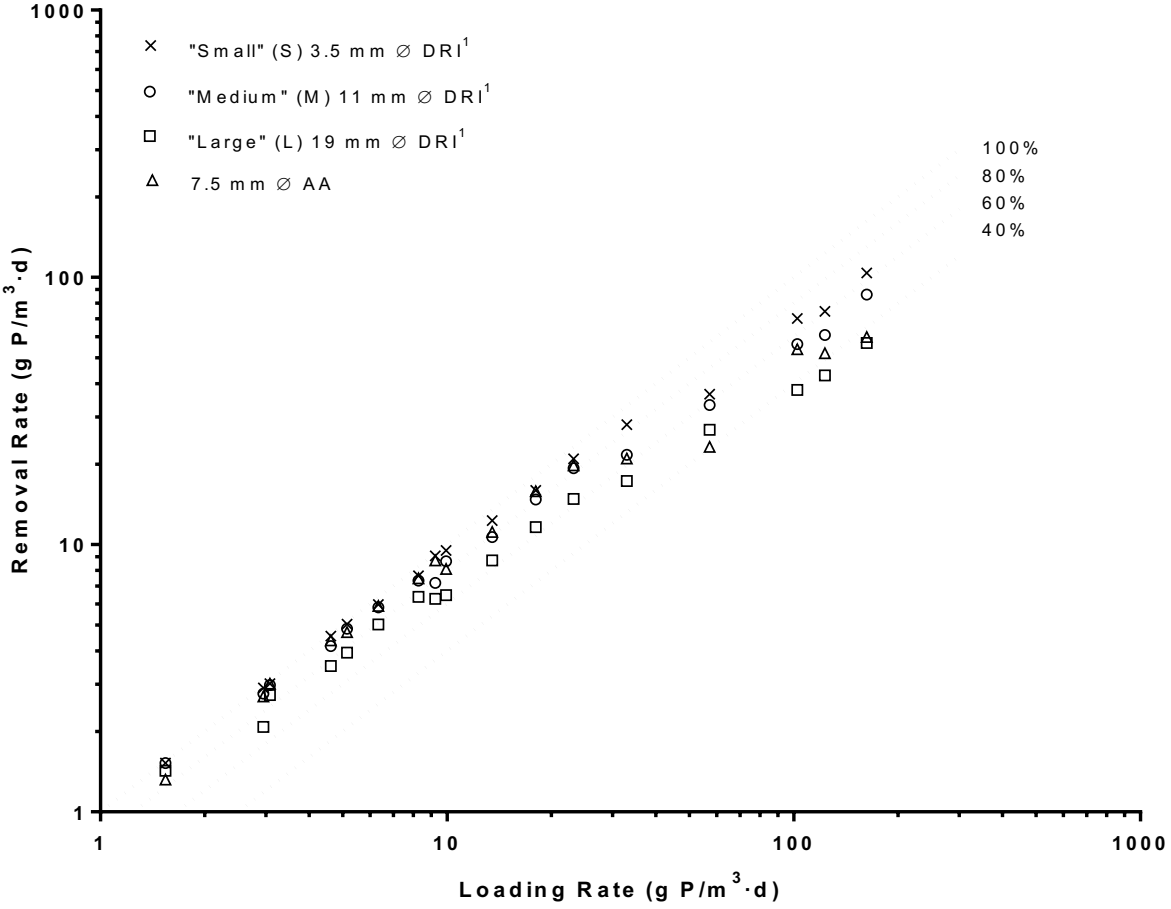

Figure 5.5. Influent loading rate v.s. removal loading rate of synthetic wastewater columns at log10 scale of DRI[1] (3.5, 11 and 19 mm) and AA (7.5 mm)

During the period of the column study, the amount of phosphorus removed by the columns was calculated and is presented in Appendix C with 2.18, 1.82, 1.22 and 3.13 mg P/g media for 3.5, 11, 19 mm DRI and 7.5 mm AA, respectively. Comparing to the P retaining capacity values obtained from the batch test in chapter 4, these values are considerably higher than the maximum P capacities from batch test results with a higher initial P concentration of 45 ppm (0.7 mg P/g media). This suggests that different removal mechanisms are dominant under column loading conditions. It is hypothesised that crystal growth plays a larger role in the column operation and suggests the potential for significantly higher media removal capacity than has been measured during the first year of column operation.

Municipal lagoon effluent wastewater

A column study was conducted for 34 days with municipal lagoon effluent using four types of media: 11 mm DRI[1], 12.5 mm DRI[2], 7.5 mm AA and 10 mm pea stone with the same column dimension as the synthetic column study (see

Figure 5.6). In this study, media were mixed with average diameter 10 mm pea stone at 1:1 volume ratio. Pea stone was also used as a blank control column and did not exhibit any P retaining capacity. The study period was divided into four phases with HRT increasing from 0.5 to 1.0 to 3.0 hrs in the first three phases at C_0 = 4 mg P/L and T=23°C, while temperature was lowered to 4°C in the fourth phase at HRT=3.0 hrs and C_0=4 mg P/L.

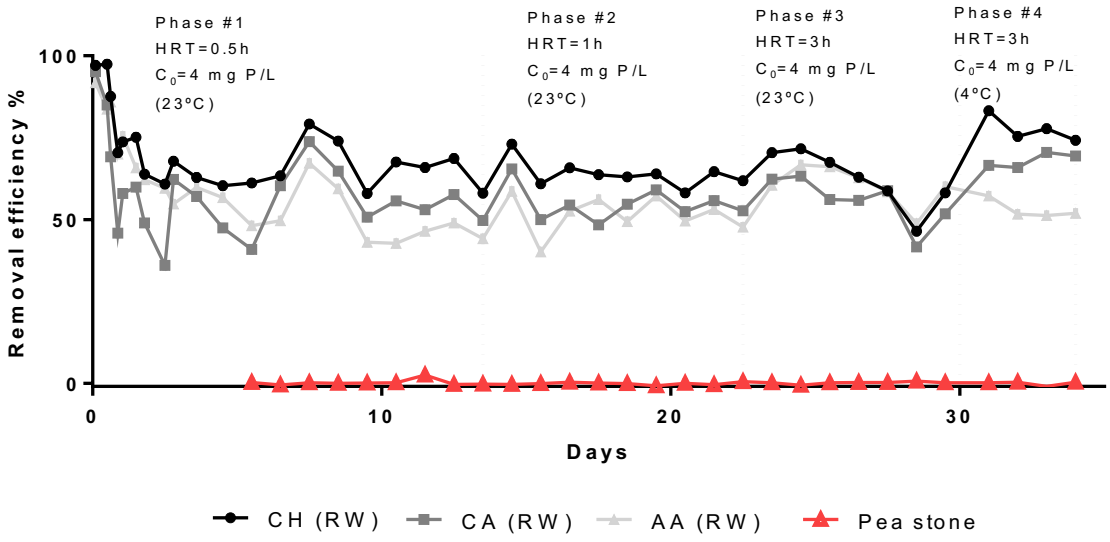

Figure 5.6. Removal efficiency for a 34 days long municipal lagoon wastewater column study (RW: real wastewater; CH: 11 mm DRI[1], CA: 12.5 mm DRI[2], AA: 7.5 mm AA, Pea stone: 10 mm)

From the figure, the trend in removal efficiency was consistent between each media and generally similar between different operation conditions (C_0 = 4, HRTs from 0.7 – 5 h). DRI[1] exhibited an average 66% removal efficiency, DRI[2] 57% average removal efficiency and AA 54% average removal efficiency. When compared with the synthetic solution column study, in phase #1, CH (DRI[1] 11 mm) and AA of synthetic wastewater were slightly lower than the lagoon effluent wastewater study, with an average efficiency of 58% and 41%, respectively. In phase #3, the two column studies had close removal efficiency with 63% and 61%. In phase #3 and #4, under 23ºC and 4ºC running conditions, the lagoon effluent column actually performed better at colder temperature which could suggest that lower temperature promotes crystallization due to a decrease of phosphate solubility and does demonstrate that the technology is effective under cold-climate conditions.

Results from the lagoon effluent column study are presented in Table 5.3 along with comparison to equivalent operating conditions from the synthetic solution column study. Removal efficiency between the lagoon effluent and synthetic solution columns were similar under the conditions tested, even though the lagoon effluent columns contained 50% non-reactive pea stone. This indicates that 1) DRI[1] performs better than DRI[2]; 2) DRI works under both synthetic and real wastewaters; 3) the percentage of active media has marginal effect on column removal efficiency at low loading rates; 4) lower temperature increases column performance, possibly by decreasing phosphate solubility and increasing crystallization.

Table 5.3. Summary of lagoon effluent column study with comparison to synthetic solution columns

Removal efficiency	C_0=4 mg P/L HRT=0.5h			C_0=4 mg P/L HRT=1h			C_0=4 mg P/L HRT=3h		
	DRI[1]	DRI[2]	AA	DRI[1]	DRI[2]	AA	DRI[1]	DRI[2]	AA
Real wastewater 50% media	63.6 (5.2)%	53.3 (3.3)%	45.1 (2.6)%	63.9 (4.1)%	54.7 (5.1)%	51.6 (5.7)%	62.2 (8.8)%	55.7 (7.4)%	55.8 (6.1)%
							75.8 (1.8)% (4ºC)	68.6 (2.4)% (4ºC)	51.6 (0.4)% (4ºC)
Synthetic wastewater 100% media	58.4 (4.1)%	n/a	41.2 (6.5)%	n/a			68.3 (3.7)%	n/a	61.2 (1.2)%

Estimated lifespan of DRI media filter

In order to estimate lifespan of DRI media filter in field applications, the maximum P retaining capacity obtained from the 1 year synthetic column study was used of 1.82 mg P/g media for 10 mm DRI[1]. The minimum hydraulic retention time has been determined with a design flow rate 1 m^3/d and maintaining an 80% removal rate. Table 5.4 summarized the life spans of DRI filter based on four typical wastewater strengths (stormwater, residential, septic tank effluent and dairy wastewater) with a flowrate of 1 m^3/d. Medium size DRI media (11 mm) was chosen as the optimum media size that can reduce clogging potential in field applications while maintaining a fairly high P removal rate. For P retaining filters treating stormwater, residential sewage, septic tank effluent and dairy wastewater with minimum HRTs (80% removal rate, based on Figure 5.4 and its linear extrapolation result) and 10 years lifespan, the filter volumes were estimated to be 0.24, 4.69, 15.3 and 36.2 m^3 respectively.

Table 5.4. Minimal estimated life spans and HRTs of DRI filter (using 11 mm DRI[1])

Wastewater sources	Storm water	Residential	Septic tank effluent	Dairy
Phosphorus concentration	0.13 - 0.3 mg/L(International Stormwater BMP Database, 2004)	3 - 9 mg/L (Youcai, 2016)	12 - 16 mg/L (Crites and Technobanoglous, 1998)	21 - 98 mg/L (Danalewich et al., 1998)
Minimum HRT	3 h	3.8 h	5.8 h	9.5 h
Flowrate (m^3/d)	1	1	1	1
Filter volume (m^3)	0.24	4.69	15.3	36.2
Life span (years)	10	10	10	10

1 m^3/d is the typical flow rate of septic effluent and dairy wastewater and it is used as design flow rate in the table. For storm water and residential wastewater which experience higher flowrate, the volume is considered the filter volume per m^3/d and the estimated life span and HRT keeps the same.

The minimal HRT is to maintain an 80% removal rate which referred Figure 5.4 and its linear extrapolation.

5.6. CONCLUSIONS AND RECOMMENDATIONS

Three media sizes of DRI[1] (3.5, 11 and 19 mm) and one media size of AA (7.5 mm) were evaluated in a 315 days column study utilizing synthetic solution with P concentrations varying from 2-10 mg/L and HRT varying from 0.7 to 15 hrs. HRT required to achieve 80% removal increased with increasing media size and concentration. Among three DRI[1] media sizes, 11 mm DRI[1] is recommended for future field studies due to its fairly high removal rate and low clogging potential. 7.5 mm AA had similar performance as medium size DRI[1] (11 mm), with bed porosity 45% and 52% respectively. A 34-d column study evaluating P-augmented municipal lagoon wastewater exhibited comparable removal efficiencies to the synthetic column tests as well as demonstrating that low temperature operation (4°C) improves the removal efficiency, possibly by promoting crystal growth. Filling columns with a 1:1 ratio of media: pea stone showed little effect on removal efficiency.

The minimum P retention capacity of the columns after 315- days of continuous dosing was found to be 1.82 mg P/g for medium size (11 mm) DRI[1]. Minimum volume for a 10-y filter life span was estimated at an 80% removal rate for stormwater, residential, septic tank effluent and diary, respectively, to be: 0.24, 4.69, 15.3 and 36.2 m^3.

In conclusion, the DRI media size, influent phosphorus concentration and HRT control the performance of the column. These will be important design factors for phosphorus reduction applications. In this study, the columns did not reach their maximum P retaining capacity due to time constraint, therefore the capacity measured is a minimum value and highly conservative. Future research should include longer-term pilot studies to

achieve column maximum capacity, pilot and field-scale studies with real wastewater as well as pilot and field media regeneration studies.

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CHAPTER 6 : CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

Phosphorus retaining filter media direct-reduced iron was thoroughly investigated to develop a fundamental understanding of P removal performance including maximum P retaining capacity and column removal efficiency. The main conclusions that were drawn from this work are the following:

1. DRI has density (3.22 g/cm^3), surface area (0.33 m^2/g), porous surface structure (< 15 μm) and high metallic content (> 85%);
2. Phosphorus influent concentration limits the media phosphorus retaining capacity in batch assays to a plateau of approximately 3000 mg/L and a maximum retention capacity of 21 mg P/ g DRI.
3. A primary removal mechanisms of phosphorus from solution by DRI media was shown to be ferric phosphate crystal formation by SEM/EDS imaging, while jar test isotherms also suggest chemical adsorption as an important mechanism;
4. The electrochemistry reaction (iron dissolving) on the DRI surface consumes hydrogen, which caused pH increase in batch (pH 10.20) and column studies (pH 7.28);
5. Saturated DRI media was shown to achieve 100% capacity recovery with 0.05 M Fe^{3+} or 0.4 N H^+ solutions. However, a maximum phosphorus recovery of 37.6% was achieved with 1.2 N H^+ solution.

6. To maintain an 80% P removal efficiency in column operation, minimum HRTs for 3.5 mm, 11 mm, 19 mm DRI and 7.5 mm AA were 4.4, 5.1, >15 and 3.9 h, respectively, for influent P concentration of $\leq$ 10 mg/L.
7. Column studies with synthetic P solution and municipal lagoon effluent had similar performance at the same operating conditions.
8. Media filling percentage showed little effect on removal efficiency under the same HRTs.
9. Filter volumes per m^3/d capacity and a 10-year life span at 80% removal efficiency has been estimated for stormwater, residential wastewater, septic tank effluent and dairy farm wastewaters, respectively to be: 0.24, 4.69, 15.3 and 36.2 m^3, respectively.

6.2. RECOMMENDATIONS

The following recommendations are intended to assist researchers working on topics which were presented in the thesis in order to expand the knowledge of DRI as phosphorus retaining filter media:

- Investigation on pH effect to the maximum P retaining capacity of DRI media should be explored.
- Run column studies to saturation to determine ideal design capacity.
- Conduct field studies to determine long-term actual design capacity and to evaluate fouling and clogging issues on filter lifespan
- Conduct further media regeneration and P recovery studies at pilot to field scale to optimize the processes.

APPENDIX A: BATCH STUDY EQUILIBRIUM

Figure 7.1. below showed that the batch assays concentrations with initial P concentration of 60, 250, and 450 ppm in an elapsed time scale.

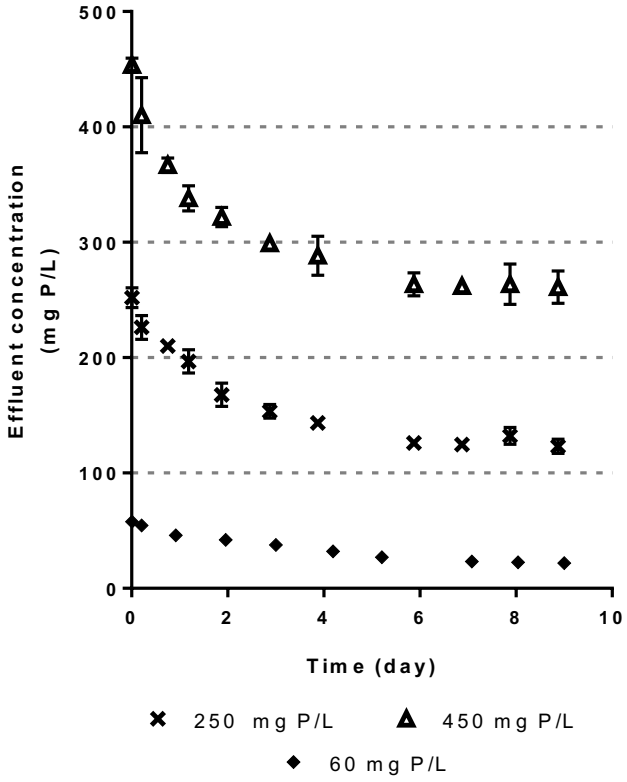

Figure 7.1. Batch assays concentrations in an elapsed time scale

APPENDIX B: TRACER STUDY OF SYNTHETIC COLUMNS

Tracer study was conducted on synthetic column with KBr salt to investigate short circuiting and confirm calculated HRTs. The background conductivity was 41.6 µS/cm. The influent conductivity was dosed up to 3.59 MS/cm and pumped into upflow columns (1 MS/cm = 1000 µS/cm) with flowrate 1.4 ml/min. The effluent was collected from two outlets (A & B) of four synthetic columns (S, M, L and A) every 30 mins for 25 hours to analyse conductivity. Figure 7.2 represented the conductivity increase with time.

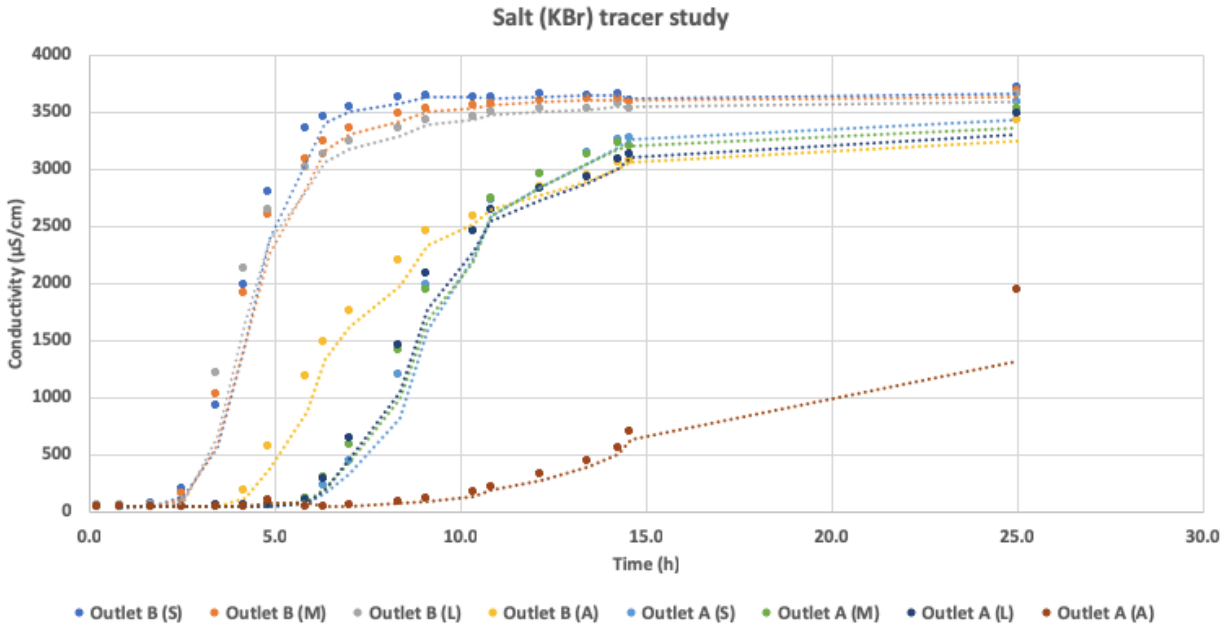

Figure 7.2. Tracer study-effluent conductivity of A and B outlets of synthetic columns

The finishing of break through segment (the starting of plateau) was considered as real hydraulic retention time. From the figure, A outlets appeared to have two folds of HRTs as B outlets. the B outlets of S (DRI 3.5 mm), M (11 mm) and L (19 mm) column

encountered break through the earliest which represented to be ~8 h. The calculated HRTs for outlet B of DRI columns were 9.7, 7.6 and 6.7 h respectively. The A outlets of S, M and L columns met break through later with ~15h. The theoretical HRTs for outlet A were 19.4, 15.3 and 13.5 hours. It seemed the theoretical HRTs were valid in terms of representing real situations and there was no short circuiting occurred. For activated alumina column, it seemed the effluent conductivity did not reach influent conductivity within 25 hours. It was suspicious that the activated alumina interfered with K^+ and Br^- which delayed the presence of ions in the effluent.

APPENDIX C: PHOSPHORUS CONCENTRATION COMPARISON BETWEEN OUTLET A & B

The outlet B phosphorus concentration was also collected over time during six of the running conditions (C_0 = 2 mg P/L, HRT = 15, 7.5, 5 and 2.5 hrs; C_0 = 4 mg P/L, HRT = 0.7 and 5 hrs). The data was compared to outlet A effluent under same running conditions in Table 7.1. From the table, it is observed that the P concentration from outlet B is similar at low loading rates (C_0 = 2 ppm, HRT = 5 – 15 h). When the loading rate increased, the effluent from outlet B showed lower removal efficiency compared to outlet A. With the larger size media, this trend became more pronounced. The outlet B had half the hydraulic retention time than the outlet A, which was confirmed through tracer testing. At low loading rates, high removal rates were maintained, which indicates that the HRT (5 h to 15 h) under relatively low influent concentration < 2 ppm is sufficient to maintain high removal efficiencies (> 80%). When HRT was reduced to less than 5 h or with higher influent concentration > 2 ppm, the removal efficiency from outlets A & B exhibited differences. Similar observation was also showed in Figure 5.4 (a), (b) and (d): within the blue area, the change was not rapid, and somehow flat. When it was in the yellow, grey and red areas, the removal efficiency appeared to be more rapid.

Table 7.1. Phosphorus removal efficiency from outlet A and outlet B (SD) (steady state)

	Outlet A (Top)				Outlet B (Middle)			
Removal efficiency % (SD)	S	M	L	A	S	M	L	A
HRT=15h/7.5h C_0=2 ppm	99 (0.4)	99 (0.6)	92.6 (2.5)	85.7 (11.6)	98.4 (4.1)	98.5 (0.6)	97.8 (1.2)	93.7 (4.5)
HRT=7.5h/3.75h C_0=2 ppm	97.9 (1.0)	96.8 (1.6)	88.9 (4.4)	97.9 (1.1)	97.4 (1.4)	94.3 (3.2)	94.3 (3.4)	97 (1.6)
HRT=5h/2.5h C_0=2 ppm	98.2 (0.6)	90.3 (2.1)	76 (9.3)	94.8 (7.0)	95 (5.6)	87.7 (5.7)	77.4 (10.5)	95.6 (3.7)
HRT=5h/2.5h C_0=4 ppm	76.5 (3.5)	68.3 (3.7)	58.1 (4.0)	61.2 (1.2)	63.1 (2.1)	61.2 (4.7)	58.5 (2.7)	46.8 (3.8)
HRT=2.5h/1.25h C_0=2 ppm	98.1 (1.1)	77.8 (6.9)	67.7 (4.2)	94.4 (4.5)	94.9 (5.0)	77.9 (6.0)	62.4 (15.0)	82.9 (9.0)
HRT=0.7h/0.35h C_0=4 ppm	61.9 (3.8)	57.4 (4.1)	45.4 (6.3)	38.6 (6.5)	59 (4.1)	54.2 (5.1)	38.7 (6.6)	26.2 (6.2)

APPENDIX D: THE CALCULATION OF PHOSPHORUS RETAINING CAPACITY OF SYNTHETIC COLUMN

Over 315 days, the amount of P retained per mass DRI media in synthetic column studies was calculated via the equation showed below:

$$q(P) = \frac{\sum_{i=1}^{n}(C_0 - C_i)Q_i}{m(DRI)} \qquad \text{Equation 7.1}$$

where C_0 =initial concentration (mg P/L)

C_i =effluent concentration (mg P/L);

Q_i =flowrate (L/d) 2, 4, 6, 12.1 and 43.2 L/d;

n =number of days operated, 315;

$q(P)$ =phosphorus retaining capacity per mass DRI media (mg P/g DRI);

$m(DRI)$ =mass of DRI/AA media in the column (g).

The results for four medias were utilized in synthetic column studies were listed below:

Table 7.2 Phosphorus removed by four columns

	3.5 mm DRI[1]	11 mm DRI[1]	19 mm DRI[1]	7.5 mm AA
Mass of P retained by the column (mg P)	6906.22	6092.16	5037.07	5704.27
Mass of media in the column (g DRI)	3170.22	3352.88	4126.28	1824.93
Capacity achieved (mg P/g media)	2.18	1.82	1.22	3.13