PHOSPHORUS REMOVAL FROM SMALL-SCALE WASTEWATER

APPLICATIONS USING ALUM SLUDGE

by

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LIST OF ABBREVIATIONS

WTP	Water Treatment Plant
ODS	Oven Dried Alum Sludge
GAC	Granular Activated Carbon
ADS	Air Dried Sludge
FDS	Freeze Thaw Dried Sludge
CKD	Cement Kiln Dust
BFS	Blast Furnace Slag
P	Phosphorus
Max	Maximum
TP	Total Phosphorus
OP	Orthophosphate-Phosphorus
PP	Particulate Phosphorus
RSSCT	Rapid Small Scale Column Test
ASTM	American Society of Testing Materials
EBCT	Empty Bed Contact Time
FT-IR	Fourier Transform Infrared Spectroscopy
EGME	Ethylene Glycol Monoethyl Ether
SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristics Leaching Procedure
USEPA	United States Environmental Protection Agency
APHA	American Public Health Association
AWWA	American Water Works Association
WEF	Water Environment Federation
BOD	Biological Oxygen Demand
MDL	Method Detection Limit
ANOVA	Analysis of Variance
XRD	X-Ray Diffraction
IR	Infrared Spectroscopy
EEC	Expected Environmental Concentration
RQ	Risk Quotient
NOEC	No Observed Effects Concentrations
BCF	Bioconcentration Factor
TRV	Toxicity Reference Value
P.E.	Population Equivalent
LECA	Light Expanded Clay Mineral
DFO	Department of Fisheries
SYSCO	Sydney Steel Corporations

LIST OF SYMBOLS

d_{60} Smallest size of sieve through which 60% of the material passes, L

Q   Adsorption density, M/M

K_d Freundlich distribution coefficient

n   Freundlich coefficient for exponent

Ce   Equilibrium coefficient

K   Langmuir adsorption constant

LC_{50} Lethal concentration at which 50% of the species dies, M/L^2

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ABSTRACT

Phosphorus removal for small-scale wastewater applications were investigated using physical chemical methods. Adsorption appeared to be the most viable technical solution for these applications. In particular, adsorption was studied using a value-added adsorbent, alum sludge. Alum sludge, a waste residual generated in water treatment utilities, was used in this research for treatment of phosphorus, in particular orthophosphate. Bench scale experiments were designed to evaluate the effectiveness for phosphorus adsorption and coagulation. Tests were conducted on both deionized water spiked with orthophosphate and wastewater (secondary municipal effluent, effluent from biofiltration process and aquaculture process water) using oven dried alum sludge (ODS). Coagulation experimental results were compared to adsorption process. Adsorption being a surface phenomenon was also studied in oven dried alum sludge using specific surface area, scanning electron micrography, x-ray diffraction, IR and ramans spectroscopy. At the end of these experiments, the residuals generated from treatment of small-scale wastewaters were studied for leachability of aluminum to address issues for environmental management.

The ODS was effective in adsorbing orthophosphate, and was comparable to other conventional and emerging adsorbents of orthophosphates. Adsorption kinetic studies investigated the effect of pH, initial phosphorus concentrations (P_i) and particle sizes on the effluent phosphorus concentrations (P_e) in batch adsorption systems and their effect on breakthrough pore volumes in a fixed bed column system. Freundlich adsorption isotherms were mostly effective in describing partitioning between solid and liquid phase. Though an influent pH 5 was found to be the most suitable pH tested, ANOVA test found the effect of pH to be insignificant on P_e and breakthrough pore volumes for high Pi at 95% level of significance. Phosphorus removals were equally effective for both P_i tested. However breakthrough pore volumes for high P_i were lower than that of low P_i. Fine particles were found to remove phosphorus better than coarse particles. Alum sludge was also effective in removing phosphorus from small-scale wastewaters, even better than that of deionized water. ODS was more effective for adsorbing orthophosphate than other types of phosphorus.

Coagulation process tested for phosphorus removal from small-scale wastewaters was found to be ineffective. Changes in alum sludge concentrations and pH also could not improve the performance. Adsorption appeared to be more effective process than coagulation for small-scale wastewater applications. In terms of operation and maintenance, adsorption also appeared to be appropriate for small-scale applications.

Scanning electron micrography indicated the possibility of micropores, supported by high specific surface area (>3000 m^2/g). Oven dried alum sludge was amorphous in nature as evidenced from X-ray diffraction experiments. Spectroscopic tests indicated the possibility of OH⁻ ion being replaced by orthophosphate ions (H_2PO^{4-}, HPO_4^{2-} and PO_4^{3-}).

The residuals generated during phosphorus treatment of wastewater were further tested for leachability in land based and surface water based disposal options. Toxicity characteristic leaching procedures (TCLP) tests conducted on these residuals observed a reduction in aluminum and manganese leaching indicating lower risk imposed for land based disposal options than alum sludge disposal. Ecological risk assessment of aluminum toxicity from surface water based disposal of these residuals also found reduced risk imposed on aquatic habitat from these residual disposals.

1.0 INTRODUCTION

1.1 Background of the Available Technology

Phosphorus (P) removal is considered as a major challenge in wastewater treatment, particularly for small-scale wastewater treatment systems. Appropriate and effective technology has always been an important consideration for small-scale wastewater treatment system. Processes available for P-treatment are generally classified into three general categories of chemical, physical or biological-based treatment systems. Among physical chemical methods, phosphorus removal is achieved using ion exchange (Zhao and Sengupta, 1998; Liberti et al., 2001; Haron et al., 1997), dissolved air flotation (Jokela et al., 2001; Kato et al., 1993; Penetra et al., 1999), and membrane filtration (Dietze et al., 2002; Yu et al., 2000; Gnirss and Dittrich, 2000). Filtration has been used either alone or in conjunction with a coagulation process as a means to remove phosphorus from wastewater (Xie et al., 1994; Andersson et al., 1992; Jonsson et al., 1997). High rate lamella sedimentation has also been attempted in some studies (Zeghal et al., 1998; Rogalla et al., 1992; Buer, 2003). Among the various physical chemical methods, coagulation with chemical precipitation and adsorption are the most common techniques being used for removing phosphorus. Enhanced biological methods for removing phosphorus are also used with success (Louzeiro et al., 2002; Wareham et al., 1995). Wetland treatment systems, combining biological uptake with P adsorption, are also used with some success, particularly for agriculture and residential wastewater treatment (Mitsch and Gosselink, 2000).

1.2 Problem Identification

Research on phosphorus removal from wastewater to date is case specific and concentrated on either biological treatment technologies or chemical methods such as coagulation/precipitation processes. For small scale applications (e.g., aquaculture) biological methods may not be appropriate for phosphorus removal because of the low carbon concentrations, which increases cost and time involved in biological methods (Park et al., 1997; Commonwealth Technology Inc., 1999). Alternatively, physical-chemical methods can offer advantages for small industries because of lower initial costs involvement (Commonwealth Technology Inc., 1999). These methods are also easier to use and do not require high level of expertise to maintain. Physical-chemical methods can also accommodate recycling sludge to reduce further costs involved in handling sludge. However, finding an effective and feasible material is a significant challenge in physical chemical approach. This problem has not been addressed so far as a complete solution. The key problem is to find a suitable material, which is easily available and effective to remove phosphorus from small-scale wastewater applications.

Regulatory control on phosphorus disposal is evident all over the world in recent years (Department of Justice, 2004; Environment Canada, 2000; USEPA, 2000; Bagyinszki and Vimola, 2000). Strict regulatory requirements decreased the permissible level of phosphorus concentration in wastewater at the point of disposal. This has made it very important to find appropriate technological solution for treatment of wastewater prior to disposal, especially for small-scale wastewater.

1.3 Alum Sludge as a Phosphorus Adsorbent

Residual management is considered very important, as there are considerable amounts of residuals and biosolids generated due to anthropogenic reasons (USEPA, 1999a; Cornwell et al., 2000). Alum sludge, a residual generated in the coagulation process in a water treatment plant is one such type. The reuse of alum sludge in other applications is being considered by many researchers in recent years (Chu, 1999; Chu, 2001; Sujana et al., 1998). Divalent and trivalent cation based materials are known to be effective for phosphorus removal (Metcalf and Eddy Inc., 2003). Therefore, aluminum based residuals (i.e., alum sludge) are a viable option for being an effective phosphorus removal material. Alum is typically effective in phosphorus removal in chemical precipitation process (Aguilar et al., 2002). Therefore, use of alum sludge can be effective for phosphorus removal. Alum sludge is typically known to be a mixture of various forms of aluminum hydroxide (Wang et al., 1992). Aluminum hydroxide is known to be very effective as a phosphorus adsorbent (Galarneau and Gehr, 1997). Air dried alum sludge has also been attempted in a limited manner by some researchers with success (Kim et al., 2003a; Baldwin et al., 1974). Therefore alum sludge has high possibility of adsorbing phosphorus. However, the use of waste material (alum sludge) not only can provide low cost appropriate technological alternative for small-scale applications, but also reduce hazard and cost related to the disposal of large amount of alum sludge. Water treatment plants are widely spread all over the world. Alum sludge would therefore, most likely be available in many parts of the world. Therefore, alum sludge can be widely adopted as a phosphorus adsorbent.

2.0 RESEARCH HYPOTHESIS AND OBJECTIVES

2.1 Research Hypothesis

The primary research hypothesis was that oven dried alum sludge was an effective

adsorbent for phosphorus. The secondary hypotheses were: adsorption was the primary

mechanism for removal of phosphorus using oven dried alum sludge; adsorption of

orthophosphate on oven dried alum sludge was comparable to other conventional

adsorbents of phosphorus; adsorption of phosphorus on oven dried alum sludge would be

more effective than that of coagulation followed by flocculation and sedimentation; and

leaching of various contaminants from oven dried alum sludge after adsorption of

phosphorus would be minimal.

2.2 Objective of the Research

Based on the hypotheses listed above, the overall objective of this research was to

determine the effectiveness of oven dried alum sludge for physical chemical processes to

remove phosphorus. It was the intent of this work to apply this technology to small-scale

applications, although results of this research could be more broadly applied where

appropriate. The specific objectives of this study were:

- To investigate the effectiveness of oven dried alum sludge for adsorption of
  orthophosphate from deionized water and small-scale wastewaters using bench scale
  experiments;
- To compare the adsorption of orthophosphate on oven dried alum sludge to other
  conventional adsorbents;

- To study the possibility of leaching contaminants from oven dried alum sludge during adsorption of phosphorus;

- To study the effect of key operating parameters on the adsorption of phosphate on oven dried alum sludge;

- To investigate phosphorus removal using oven dried alum sludge in bench-scale experiments using coagulation as process alternate;

- To compare the phosphorus removal using adsorption with coagulation process;

- To characterize the surface of oven dried alum sludge for understanding the adsorption behaviour; and

- To investigate the leachability of the residuals generated from adsorption of phosphorus on oven dried alum sludge.

2.3 Originality of the Research

Alum sludge has been evaluated previously for phosphorus removal by some researchers (Kim et al., 2003a; Huang and Chiswell, 2000; Baldwin et al., 1974), however, these studies were conducted on air dried alum sludge and found to be effective. These studies used chemical precipitation and adsorption as process alternate for alum sludge. However, air drying required long time and large area. Oven dried (105^0 C for 24 hours) alum sludge has not been used for P-removal. The research conducted during this project would provide a complete rationale background for the used alum sludge for reuse in small-scale applications.

Alum sludge, more specifically oven dried alum sludge, was a new material in term of its application and reuse. There were a few studies conducted on the engineering properties of alum sludge (Wang et al., 1992; Zhao and Bache, 2001). However, there has not been characterization of oven dried alum sludge surfaces for understanding adsorption behaviour. The use of many surface characterization experiments during the project to understand characteristics and features of alum sludge surfaces and its role in possible phosphorus adsorption mechanism was original and first of its kind for alum sludge.

The use of oven dried alum sludge, like any adsorbent; for removal of phosphorus would generate residual after oven dried sludge was exhausted. As the idea of using alum sludge for removal of phosphorus was new, this project examined strategies to manage with these new types of residuals generated after adsorption of phosphorus in alum sludge. The idea of waste management contributed to the assessment of sustainability of this technology.

2.4 Organization of Thesis

Chapter 3 reviews the literature and summarized various physical chemical treatment processes for the removal of phosphorus in small-scale wastewater. This chapter prepares the readers in terms of context, necessity and application of this research project.

All experimental work in this research used bench scale reactors to model the physical and chemical treatment processes. Prior to discussing any results, Chapter 4 presents a detailed description of the experimental procedures used for the bench-scale system. Also

discussed in Chapter 4 are the statistical procedures common to majority of the research. This chapter also includes the analytical techniques and quality control issues used in several methods.

There could be various types of materials used for phosphorus removal as an adsorbent. Chapter 5 discusses results on batch adsorption tests to evaluate relative phosphorus removal behaviour in alum sludge and other conventional phosphorus adsorbent.

Oven dried alum sludge, appeared to be an effective phosphorus adsorbent from Chapter 5 are used in Chapter 6 for further kinetic studies. Static batch adsorption test results are discussed in Chapter 6 to understand the adsorption kinetics of phosphorus onto oven dried alum sludge. This chapter discusses the effect of pH, initial phosphorus concentration and particle size on the phosphorus adsorption behaviour of oven dried alum sludge. The effectiveness of phosphorus removal behaviour is discussed in terms of effluent phosphorus concentration and adsorption density. This chapter used both deionized water spiked with orthophosphate and small-scale wastewaters.

Chapter 7 discusses adsorption kinetics in dynamic fixed bed column. Similar to Chapter 6, the kinetic studies investigated the effect of pH, initial phosphorus concentration and particle size on the phosphorus removal behaviour from deionized water spiked with phosphorus. This chapter also included investigation on small-scale wastewater. The results also looked at the effect of these wastewater and adsorbent characteristics on the

aluminum and organic matter leaching during adsorption of phosphorus on oven dried alum sludge.

In Chapter 8, bench scale test (jar test) results are discussed for the use of coagulation followed by flocculation and sedimentation for removal of phosphorus. This Chapter includes the comparative phosphorus removal capability with conventional coagulants. This Chapter also discusses the comparative advantages and disadvantages of coagulation with adsorption as process alternate.

Chapter 9 examines the surface characteristics of oven dried alum sludge to understand the adsorption of phosphate on sludge surfaces. In this chapter, scanning electron microscopy, X-ray diffraction, infrared and raman specstroscopy and estimated specific surface area are used to describe the behaviour of oven dried alum sludge surfaces for adsorption of phosphate.

Finally, in Chapter 10 the management of residuals that were generated during treatment of phosphorus from small-scale wastewater in Chapter 7 are discussed. This chapter investigated the potential metal leaching ability of these waste materials in both land based and surface water disposal. The surface water leaching of aluminum was also used to investigate ecological risk assessment of these residuals.

3.0 A REVIEW OF PHYSICAL-CHEMICAL APPROACHES TO PHOSPHORUS REMOVAL FOR SMALL-SCALE APPLICATIONS

Discharges from municipal waste pollution control plants are typically noted among the major contributors of phosphorus to the receiving water (Nutt, 1991). The contributors of phosphorus emission are both point source and non-point source polluters (Figure 3-1). Phosphorus removal from point source polluters has been a concern for many years. A large number of these point source polluters are small-scale in nature. The objective of this chapter was to review various wastewater treatment process options in the context of small-scale wastewater applications including the relevance of phosphorus removal for these small-scale wastewaters. This chapter reviews various physical chemical approaches for the treatment of phosphorus from wastewater. The review compared various materials for removal of phosphorus using adsorption, coagulation, membrane and ecological treatment processes. This chapter also includes a discussion on the various physical chemical methods of phosphorus removal.
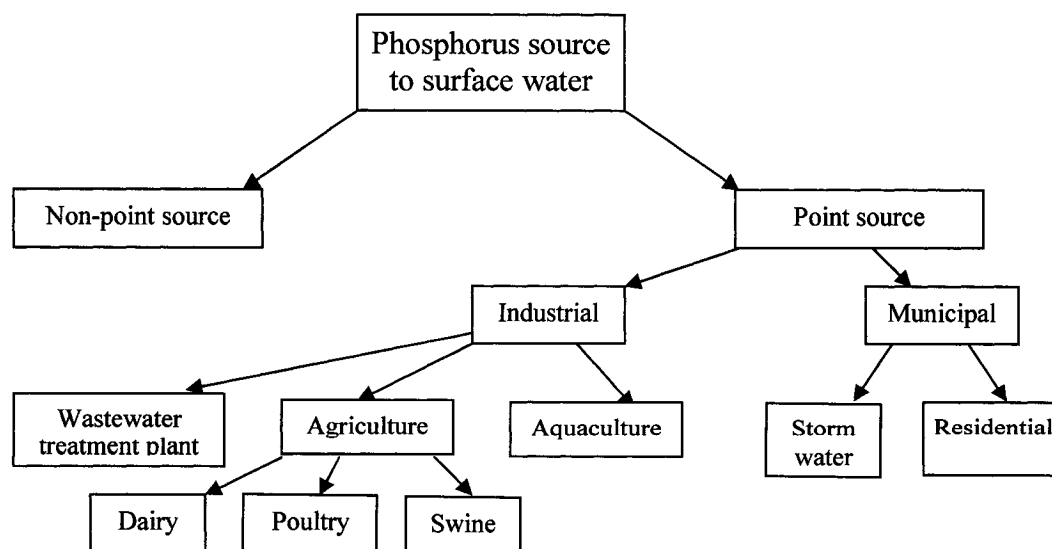
Figure 3-1. Example of various sources of point source phosphorus in surface water

3.1 Small-scale Applications

Small-scale applications (e.g., small aquaculture, dairy, poultry, and swine farms) are considered as those point source emissions of phosphorus, which contribute to significant phosphorus loads in surface water. Residential point wastewater sources for rural and decentralized communities are typical examples of small-scale applications (Crites and Tchobanoglous, 1998). Other on-site decentralized wastewater systems can also be considered as small-scale industries. In general, small-scale wastewater contributes 20% of the total wastewater generated in Canada; in Atlantic Canada, this contribution is approximately 50%. Small to medium sized industries can be characterized by having limited resources and infrastructure particularly for environmental treatment. Therefore, the major restrictions these industries have are cost and resources. However, process options that are easy to operate and maintain required for treatment of these wastewaters.

In this study, small-scale applications were considered as small municipal and aquaculture point source emissions of phosphorus, which contribute to significant phosphorus loads in surface water. The term "small-scale," in reference to wastewater applications, is often used liberally, as the definition is usually defined based on population equivalent or flow rate. European countries normally consider small-scale wastewater as less than 2,000 population equivalent (p.e.) (Table 3-1). Population equivalent is the amount and pollution of wastewaters attributed to the average value of one inhabitant (EBS, 2004). Generally, 1 p.e. is equivalent to 60 g BOD per day (Olesen, 1990). Densely populated countries like Japan consider communities of less than 10,000 to be small-scale, which is similar to the definition used by the United States

Environmental Protection Agency (Iwai et al., 1990; USEPA, 2000). In Canada, a p.e. of 600-2000 is considered as a small-scale application (Laughton et al., 1990).

Table 3-1. Definition of small-scale wastewater services by population equivalent

Country	Small-scale municipality (p.e.)	Reference
England	2000	Crabtree and Rowell, 1993; Green et al., 1998; Greaves et al., 1990
Norway	35-2000	Rusten and Eliassen, 1993; Odegaard et al., 1993; Odegaard and Storhaug, 1990
Denmark	100-2000	Jansen et al., 1993
Switzerland	1000	Boller and Deplazes, 1990
Cyprus	25-2000	Hadijvassilis, 1990
France	2000	Racault and Vachon, 1990
Yugoslavia	5000	Rismal, 1990
Japan	100-10000	Iwai et al., 1990
Canada	600-2000	Laughton et al., 1990; CCME, 2003
USA	10000	USEPA, 2000

Small-scale wastewater applications can also be defined by flow rate. Young and Koopman (1991) defined small-scale wastewater flow in United States to be less than 0.2 m^3/s. Laughton et al. (1990) considered small-scale wastewater flow rate to be 0.45 m^3/d. Crites and Tchobanoglous (1998) provided a widely acceptable flow rate of 1 Mgal/d

(0.045 m^3/s) for small-scale wastewater flow. In the present study a flow rate of 0.045

m^3/s or less will be considered to be small-scale wastewater flow. Regardless of their

flow or p.e. definition, small-scale wastewater system are typically characterized by

limited resources, infrastructure or by flow rate. Therefore, the major restrictions to

small-scale wastewater operations are cost, human resources and robust operation.

3.2 Relevance of Phosphorus in Small-scale Applications

Phosphorus can be present in both solid and liquid phases in water. The sources of

phosphorus in municipal and on-site wastewater are feces and urine. Aquaculture

wastewater also contains phosphorus from fish excreta and unused food. Small-scale

applications in the context of phosphorus have great significance in Canadian

environment.

3.2.1 Aspects of phosphorus pollution from aquaculture

Phosphorus is an essential element for living organisms. Phosphorus is required in fish

for optimum growth, feed efficiency, bone development and maintenance of acid-base

regulation (Kibria et al., 1996). Phosphorus must be provided in fish feed because of its

low availability in water. However, about 70% - 80% of the nutrients added are lost to the

environment through metabolic waste, feces and food fragments (Chambers et al., 2001).

Studies conducted in Europe and Northern America have revealed a phosphorus surplus

in most commercial feeds which is either above actual requirements; or is supplied in a

form which is unavailable to the fish (Kibria et al., 1996).

Discharge of phosphorus from fish farms and hatchery effluents have caused

eutrophication in Nordic countries, North America and Europe. Aquaculture is a rapidly

expanding industry in Canada (Chambers et al., 2001). In 1996, 53000 tonnes of finfish

and 19000 tonnes of shellfish were harvested in Canada representing a value of $350

million (DFO, 1998). Phosphorus loading from aquaculture operations in Canada is 204

tonnes/yr to inland waters and 282 tonnes/yr to coastal waters (Chambers et al., 2001).

3.2.2 On-site wastewater system

On-site treatment systems are designed to treat wastewater for one building or a small

collection of buildings. Approximately 25% of Canadians are served by on-site septic

disposal systems (Chambers et al., 2001). On-site wastewater systems treat household

wastewater that generally contains high phosphorus content from human excreta and

household waste. Conventional on-site treatment system consists of preliminary

separation of solids (e.g. septic tank), followed by soil absorption system (disposal into a

drainage field) (Crites and Tchobanoglous, 1998). In a survey of Ontario cottages, an

average of 61% of on-site treatment systems on cottage properties were not properly

designed (Dillon et al., 1986). Phosphorus retention was observed at an average rate of

72% for an influent concentration of 15 mg/L in preliminary separation and drain field

(Robertson et al., 1998). Based on that data, phosphorus concentration would still exceed

most regulatory barriers on a concentration basis. In fact, phosphorus release in Canadian

surface water and groundwater from on-site treatment systems was estimated to be 1.9

thousand tonnes annually (Chambers et al., 2001).

3.2.3 Municipal wastewater

Municipal wastewater is a leading source of phosphorus pollution in Canadian environment. In 1996, phosphorus discharge from municipal wastewater treatment plants and sewer systems were 7.9 thousand tonnes annually (Chambers et al., 2001). Surveys conducted by Environment Canada (1996) showed that 73% Canadians were served by municipal sewer systems. The municipalities having primary treatment or no treatment in Inland, Pacific coastal and Atlantic Canada accounts for 16%, 85% and 66% of the total municipalities (Chambers et al., 2001). These municipalities are mostly small in capacity. Phosphorus removal is ineffective without any tertiary treatment, and therefore, these municipalities are still likely to discharge large amount of phosphorus.

3.3 Phosphorus Removal Technologies

Phosphorus removal technologies have been developed using chemical, biological processes or a combination of both processes. Physical processes are also used as complementary technology to both the processes above. Physical processes are used to separate solids from liquid. Soluble phosphorus found in environment is mostly present as orthophosphate (Mann, 1996), which has been considered as the target for most of the treatment technologies. Chemical processes on the other hand, are used to bring soluble phosphorus to bulk phase. Once the soluble phosphorus is in the solid phase, physical processes are used for removal. Reviews on phosphonates discussed similar chemical behavior of adsorption and chemical precipitation (Nowack, 2003). Constructed wetlands, reverse osmosis or evaporation have also been used for phosphorus removal.

However, due to cost and operational limitations they are not very suitable for small-scale industries.

3.3.1 Chemical precipitation

Chemical precipitation is a reaction that causes insoluble precipitates to settle and is strongly dependent on pH, phosphorus and coagulant concentration. Precipitation of phosphorus from municipal wastewater with the addition of divalent and trivalent metal salts has been widely reported in North America and Europe (Nutt, 1991). Common metal coagulants that have been examined are iron salts (ferric chloride, ferric sulfate, ferrous chloride, ferrous sulfate), aluminum salts (aluminum sulfate, aluminum chloride, sodium aluminate, polyaluminum chloride) or calcium-based compounds (lime and gypsum) (Narasiah et al., 1994). The removal efficiencies of individual materials are different and based on their individual reaction kinetics. The reactions between the metal salts and phosphorus are complex due to the presence of different species of phosphorus in the wastewater. The generally accepted theory is that a primary reaction occurs between the metal ion and orthophosphate to precipitate the insoluble metal phosphate. Chemical reactions create different types of complexes. The simplest forms of precipitation reactions are:

$$Al^{+3} + PO_4^{-3} \rightarrow AlPO_4\downarrow \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots3\text{-}1$$

$$Fe^{+3} + PO_4^{-3} \rightarrow FePO_4 \downarrow \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots3\text{-}2$$

$$Ca^{2+} + PO_4^{-3} \rightarrow Ca_3(PO_4)_2 \downarrow \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots3\text{-}3$$

Stable precipitates of $FePO_4$ and $AlPO_4$ are created in the pH range of 5-7 (Jiang and Graham, 1998). The calcium precipitate at pH above 7 is predominantly

$Ca_{10}(PO_4)_6(OH)_2$. Generalized precipitates of Al/Fe hydroxo-phosphates are $Al(OH)_{3-x}(PO_4)_x$ and $Fe(OH)_{3-x}(PO_4)_x$. The value of x in these precipitates depends on the extent of hydrolysis and pH of the precipitation reactions. These precipitates produce large amounts of sludge. However, safe and environment friendly disposal of this sludge is a big concern for the wastewater treatment utilities.

3.3.2 Adsorption

Chemical adsorption can also be associated with chemical reactions that occur in many precipitation processes. The adsorption of phosphorus occurs when orthophosphate attaches to the surface of the adsorbent. Phosphorus adsorption may be physical or chemical in nature. Several metal coagulants (e.g., alum) are well known to exhibit strong adsorption characteristics (Eckenfelder, 1999).

In addition, waste materials those are high in divalent and trivalent metal concentration have also found to be useful phosphorus adsorbents. The materials that have been examined are blast furnace slag (Drizo et al., 2002), opoka (Johansson and Gustafsson, 2000; Johansson, 1999a), clay minerals (Ioannou and Dimirkou, 1997), activated red mud (Pradhan et al., 1998), polyacrylamides (Sherman et al., 2000), podzolised forest soil (Johansson, 1999a), zeolite (Sakadevan and Bavor, 1998), manganese nodules (Parida and Mohanty, 1998), calcium sulfate (Theis and Fromm, 1977) and other waste residual (Dayton, 2003). These adsorbents can either be added in the primary clarifier (pre-precipitation), secondary clarifier (simultaneous precipitation) or in a reactor-clarifier (post-precipitation) (Narasiah et al., 1994). Multiple point addition of

coagulants/adsorbents to allow combinations of pre-simultaneous and post-precipitation has been found to be successful in reducing the overall chemical requirement.

3.3.3 Biological phosphorus removal

Biological treatment is one of the most widely used treatment alternative for phosphorus removal. The uptake of phosphorus in excess of metabolic requirements is a well documented survival mechanism for many bacteria (Barnard, 1975). Although phosphorus uptake in the activated sludge process is very complex, nitrate removal in anaerobic stage is known to be a precondition for effective biological phosphorus uptake (Mann, 1996). The presence of volatile fatty acids in wastewater is needed for biological phosphorus removal (Randall et al., 1992). Alternative anaerobic and aerobic reactors for micro organisms provided the effectiveness of phosphorus removal. Biological treatment reduces the waste generated during the treatment process. However, biological wastewater treatment systems are notorious for their effectiveness and stability (Park et al., 1997).

3.3.4 Recirculating media filter

Recirculating biofilters are normally used to treat septic tank effluents. It provides advanced secondary treatment of settled wastewater. In general, sand and/or gravel are used to treat wastewater. Chemical adsorption onto the media surface can play a significant role on removal of phosphorus (USEPA, 2004). However, a limited number of adsorption sites often limit phosphorus removal after a certain period of time. Sand and gravel as commonly used filter media are not known to be efficient adsorbents of

phosphorus. Studies conducted on sand, crushed glass, peat and geotextile biofilters showed 6.2%-12.5% phosphorus removal (Hu and Gagnon, 2005).

3.3.5 Membrane processes

Membrane treatment processes provide a physical barrier for removing sub-micron particles (Lozier et al., 1997). Membrane is a fast growing technology in wastewater treatment (Hillis, 2000). Small wastewater systems require simple solutions which are easy to operate and maintain. Membrane technologies can provide simple, yet elegant, treatment solutions that are easy to operate. Though membrane technology is not common in small-scale wastewater treatment, it has potential for development as phosphorus removal alternative for small wastewater systems. For phosphorus removal, the use of membrane was reported in a limited fashion (Dietze et al., 2002; Yu et al., 2000; Gnirss and Dittrich, 2000). In particular, microfiltration was effective in removing phosphorus from secondary municipal effluent. Membrane technology in conjunction with other chemical or biological process was observed to be effective in removing phosphorus from small-scale wastewater systems (Ratanatamskul et al., 1995).

3.3.6 Ecological removal technologies

The use of ecological technologies for removing phosphorus from wastewater has drawn considerable interest (Rectenwald and Drenner, 2000). The concept has been used in the form of wetlands (Serodes and Normand, 1999; Nnadi and Addasi, 1999; Mann and Bavor, 1993; Comeau et al., 2001), solar aquatics (Industry Canada, 1997, Teal and Peterson, 1993) and hydroponics (Soto et al., 1999; Ayaz and Saygin, 1996; Vaillant et al., 2003). Among these concepts, wetlands are the most widely used ecological

technology that has been used for removing phosphorus from wastewater. However, the required land area, costs and lack of operational history limited the acceptance of solar aquatic and other innovative treatment systems (Stephens, 1998). Ecological technologies are growing because of their robustness for treating variable wastewater streams and low reliance on high energy or chemical input.

3.4 Physical Chemical Removal of Phosphorus

3.4.1 Coagulation studies

Typically, previous coagulation studies were conducted using jar tests (Table 3-2). Although standard jar test procedures are widely recognized in the literature (USEPA, 1999b), these cited investigations were conducted on a case by case basis without using any standardized jar test procedure. Thus, comparison among coagulants can only be made on the basis of general trends rather than specific data, as mixing periods varied in rotational speed, duration and settling time. In particular, Baldwin et al. (1974) used mixing periods of five minutes at 100 rpm, five minutes at 10 rpm and settling period of 30 minutes, whereas, Aguilar et al. (2002) used mixing periods of five minutes at 200 rpm, five minutes at 20-30 rpm and settling period of 60 minutes.

In general, increasing the alum concentration results in a higher removal of phosphorus, as found by Baldwin et al. (1974) and Sherman et al. (2000). From these studies, it was evident that percentage removal increases with an increase in coagulant dose (Environment Canada, 1977). Alum sludge resulting in a similar removal pattern, required approximately ten times higher coagulant doses were required than alum

(Baldwin et al., 1974). However, usage of sludge as a coagulant would provide cost savings over other conventional coagulants for phosphorus removal. In general, the optimal pH for alum or alum sludge coagulation was in the range 5 - 6.7. The optimal alum dose observed for most of the investigations was 100 mg/L.

Table 3-2. Comparative jar test results on several coagulants on raw water

Coagulants	Initial P (mg/L)	Coagulant (mg/L)	Max. % removal	pH	Reference
Alum sludge	3.6-6.6	50-150 as Al	80	5-6.7	Baldwin et al., 1974
Alum	3.6-47.9	5- 600 as Al	60-99	5-8.2	Baldwin et al., 1974; Sherman et al., 2000; Aguilar et al., 2002; Environment Canada, 1977
Ferric chloride	1.3-47.9	0-376 as Fe	70	7.1-7.6	Sherman et al., 2000; Environment Canada, 1977
Ferric sulfate	9.7	500 Fe	100	7	Johansson and Gustafsson, 2000
Polyacrylamides	47.9	0 - 4	< 30	7.9-8.1	Sherman et al., 2000
Polyaluminum chloride	25.78	857	100	6-7	Aguilar et al., 2002
Gypsum	9	100 – 200	90	8-9	Theis and Fromm, 1977
Pickle liquor	4.5	0 –26 as Fe	50-90	5-10	Environment Canada, 1973b
Spent mine acids	5	0 – 20 as Fe	35-98	7	Environment Canada, 1973b
Stack precipitator dust	4.1	0 – 2500	25-90	9.5	Environment Canada, 1973b

Iron salts ($FeCl_3$, $Fe_2(SO_4)_3$) also provided phosphorus removal (Environment Canada, 1973a), but required slightly higher coagulant concentrations compared to alum. Gypsum has been used for removing phosphorus; however it increases pH and sludge volume. Polyaluminum chloride has been used for phosphorus removal, however, unlike alum

and iron salt, polyaluminum chloride was effective in coagulation studies under a wide range of pH and temperature, and resulted in a lower residual metal ion concentration (Harper and Rosenberg, 1995; Diamadopoulos and Vlachos, 1996). Experiments conducted in an unconventional jar test configuration showed that pickle liquor, spent mine acid leach solution, and stack precipitator dusts were capable of removing significant amounts of phosphorus (Environment Canada, 1973b). The application of coagulant aids enhanced phosphorus removal. The use of polyelectrolytes as a coagulant aid was observed to provide increased phosphorus removal (Environment Canada, 1976a).

3.4.2 Batch adsorption studies

Batch adsorption experiments under static hydraulic conditions have been reported in the literature (Table 3-3). Air dried alum sludge, limestone, blast furnace slag, activated red mud, manganese nodules and some clay minerals have shown a high adsorptive capacity for phosphorus (Kim et al., 2003a, Sakadevan and Bavor, 1998; Pradhan et al., 1998; Parida and Mohanty, 1998; Johansson, 1999a; Ioannou and Dimirkou, 1997). Higher removals were associated with either higher adsorbent concentration or lower initial phosphorus concentration. Optimal pH levels for the highest phosphorus removal varied widely for different adsorbents. For instance, optimal P removal using blast furnace slag was associated with a high pH of 10 (Sakadevan and Bavor, 1998). In comparison, manganese nodules and activated red mud showed high removal at a pH of 5-6 (Pradhan et al., 1998; Parida and Mohanty, 1998). Under optimal pH condition, blast furnace slag

achieved higher phosphorus removal than manganese nodule and activated red mud.

Opoka and different soil and sand samples did not show significant phosphorus removal.

Table 3-3. Comparative batch adsorption results on several adsorbents using synthetic water

Adsorbent	P (mg/L)	Adsorbent (g/L)	Max. % removal	pH	Reference
Alum sludge	100-4000	33	100	3.5-11	Kim et al., 2003a
Blast furnace slag	5-10000	20-100	50-90	5-10	Johansson and Gustafsson, 2000; Sakadevan and Bavor, 1998; Yamada et al., 1986
Steel furnace slag	500-10000	100	50	n. r.	Sakadevan and Bavor, 1998
Opoka	5-25	0.02	20	7-8.9	Johansson and Gustafsson, 2000; Johansson, 1999a
Activated red mud	24 – 190	2	97	5.2	Pradhan et al., 1998
Limestone	5-25	20	85	8.9	Johansson, 1999a
Podzolised forest soil	5-25	20	50	4.9-5.4	Johansson, 1999a
Soil samples	500 – 10000	100	> 50	n. r.	Sakadevan and Bavor, 1998
Zeolite	500 – 10000	100	> 50	n. r.	Sakadevan and Bavor, 1998
Manganese nodules	1.3	2 – 10	90	5.23	Parida and Mohanty, 1998
Hematite	1.3-13.8	1	n. r.	3.8-9	Ioannou and Dimirkou, 1997
Kaolinite	1.3-13.8	1	n. r.	3.8-9	Ioannou and Dimirkou, 1997
Kaolinite-hematite system	1.3-13.8	1	100	3.8-9	Ioannou and Dimirkou, 1997
Sand	2.5-160	10	<50	7.7-9.6	Bubba et al., 2003

n.r. – not reported

Particle size was not mentioned as a key experimental factor in many of the studies,

although particle size influences adsorption behavior (Sakadevan and Bavor, 1998;

Pradhan et al., 1998).

Adsorbents used for batch tests were not similar to the coagulants used for jar tests

(Table 3-2). However, the adsorbent concentrations used in batch tests were higher than

the coagulant concentrations used in jar tests. These higher adsorbent concentrations may

be associated with usage of synthetic water having high initial concentration compared to

raw water used in jar tests (Table 3-2). The timeframe used during the batch adsorption

tests was longer than the timeframe used in coagulation jar tests, as batch tests were run

for hours as opposed to minutes.

3.4.3 Fixed bed column studies

Column tests or fixed bed adsorption tests are methods for dynamic testing of

adsorbance, in which experiments were conducted to simulate full scale conditions in a

laboratory. Water is typically passed up or down through a column of adsorbent and the

phosphorus concentration is measured at the influent and effluent. The main parameters

being examined are the time and volume of wastewater processed when the effluent

concentration reaches breakthrough or a maximum effluent value. Column testing on

adsorbance of phosphorus was conducted in a limited manner (Table 3-4). Multiple

adsorbents were also used in the same column for investigations. The experimental

design for each of these studies is different, including high variability in time. No

identifiable breakthrough was observed in effluent concentrations in many of these

studies. Consequently, the comparison provided in Table 3-4 provides a general

overview of the phosphorus removal capacity of various materials. In particular, blast

furnace slag showed the best phosphorus removal characteristics, removing 95% of

phosphorus, even after 56 weeks. Alum sludge was shown to remove approximately 0-

700 breakthrough pore volumes of water with various pH levels tested (Kim et al.,

2003a). However, opoka mixed with sand showed the efficient phosphorus removal

capacity (Table 3-4). The experiment for opoka was conducted with a flow rate of 100

mL/min. Though in batch adsorption tests opoka did not show good adsorbance capacity,

opoka as a mixture of sand was found to be good when used in an adsorption column.

Though clay minerals showed efficient removal capability in batch adsorption test, light

expanded clay aggregates showed poor adsorbance in the column test. The comparison

of batch to adsorption columns demonstrates the complexity of adsorption processes and

the importance of field and/or feasibility studies that can readily scaled into practice.

Table 3-4. Comparative column test results on several adsorbents using synthetic water

Adsorbent	P (mg/L)	Column Vol. (L)	Particle (mm)	Removal	pH	Reference
Alum sludge	4.35-5.4	4	> 2.8	83% at 40 hr	6.5-7.1	Huang and Chiswell, 2000
Alum sludge	10	0.04	n. r.	0-700 b.p.v.	3-12	Kim et al., 2003a
Opoka + sand	3-20	35	0 – 4	75% at 25 day	7	Johansson, 1997
LECA* + opoka	3-20	35	0 – 4	63% at 25 day	7	Johansson, 1997
Blast Furnace Slag	10	25	0.25-4	95% at 56 week	9-11.2	Johansson, 1999b

* Light expanded clay aggregate, n.r. – not reported, b.p.v. – breakthrough pore volume

3.4.4 Pilot studies

The performance of treatment plants in full-scale testing provides more of an appropriate

evaluation under practical circumstances. It was inconclusive as to whether these

treatment plants were small scale or large scale, but it is believed that the results are

adaptable to full-scale plants of any size. The results from some of the full-scale tests

showed good phosphorus removal with conventional coagulants (Table 3-5). Different

full-scale studies are associated with variation in wastewater characteristics. Alum and

alum sludge provided similar optimum coagulant concentration and pH levels, compared

to laboratory scale investigations. Higher pH and coagulant in the plant tend to show

higher sludge generation. Ferric salts showed better phosphorus removal capabilities in

plant scale experiments compared to laboratory experiments (Tables 3-2, 3-5). Though

the concentration of coagulants and pH were not the same as the laboratory tests, similar

Table 3-5. Comparative plant results on several coagulants

Coagulants	Initial P (mg/L)	Concentration (mg/L)	Max. % removal	pH	Reference
Alum sludge	3.6-6.6	0 – 60 as Al	92	5.5-8.3	Baldwin et al., 1974
Alum	3.6-47.9	0 - 200 as Al	85-98	5.5-8.3	Baldwin et al., 1974; Sherman et al., 2000; Environment Canada, 1976b; Environment Canada, 1973c
Ferric chloride	2.3-18	8.8-20 as Fe	60-90	6.0-7.3	Environment Canada, 1976b; Environment Canada, 1974
Ferric sulfate	2.3-18	40 as Fe	83	7.0-7.3	Environment Canada, 1976b
Lime	2.3-18	125 – 200	85	7.5-8.0	Environment Canada, 1976b

removal efficiencies were obtained in plant scale experiments. However, plant scale tests

showed whether certain coagulants can be applied or not. These studies demonstrated the

applicability of laboratory based studies for estimating phosphorus removal

characteristics.

3.4.5 Full scale membrane studies

In general, there has been limited research conducted on the phosphorus removal

capabilities of membrane filtration. In Germany, researchers investigated the potential for

Table 3-6. Phosphorus treatment in different membrane treatment studies

Membrane Type	Vendor	Size (μm)	Initial P (mg/L)	Max % removal	Reference
No coagulation					
Microfiltration	DOW	0.2	0.186	67	Dittrich et al., 1996
Microfiltration	Starcosa	0.2	0.186	50	Dittrich et al., 1996
Microfiltration	Memcore	0.2	0.186	68	Dittrich et al., 1996
Ultrafiltration	Rochem	0.01	0.99-0.319	90	Dietze et al., 2002
With Ferric chloride					
Microfiltration	DOW	0.2	0.12	60	Dittrich et al., 1996
Microfiltration	Starcosa	0.2	0.12	64	Dittrich et al., 1996
Microfiltration	Memcor	0.2	0.12	71	Dittrich et al., 1996
Microfiltration	Memtech	0.2	0.16	89	Gnirss and Dittrich, 2000
Microfiltration	Membrain	0.2	0.16	89	Gnirss and Dittrich, 2000
Ultrafiltration	Rochem	0.01	0.99-0.319	87	Dietze et al., 2002

membrane filtration in removing phosphorus from wastewater (Dietze et al., 2002; Gnirss and Dittrich, 2000; Dittrich et al., 1996). Table 3-6 shows the influent and effluent phosphorus concentration during these investigations. The maximum phosphorus removal was achieved using ultrafiltration membrane (Dietze et al., 2002). Total phosphorus removals using microfiltration were documented as of 50% to 70% (Dittrich et al., 1996) and 80% to 90% (Gnirss and Dittrich, 2000). The efficiencies of membrane filtration were also attempted with pretreatment with low ferric chloride (0.3-4.5 mg/L as Fe). Dittrich et al. (1996) observed 60-70% removal of total phosphorus, indicating no significant difference with the addition of ferric chloride. Dietze et al. (2002) also observed insignificant phosphorus removal using ferric chloride (90%). However, initial total phosphorus concentration was low (1.9 – 3.2 mg/L) compared to the conventional phosphorus level (4-12 mg/L) in municipal wastewater (Crites and Tchobanoglous, 1998).

3.4.6 Ecological phosphorus removal studies

A summary of some typical ecological treatment technologies are listed in Table 3-7. There were no widely used standardized testing procedures for ecological treatment technologies. The use of different species of aquatic plants and animals often made the comparison of these technologies impossible. Wetlands were the most efficient ecological treatment technology used to treat phosphorus in municipal wastewater. Generally, wetlands can be both natural and constructed. The performance of constructed wetlands was improved by the addition of chemical process (adsorption) (Sakadevan and Bavor, 1998). However, natural wetlands relied on consumption of aquatic animals and

plants to treat phosphorus. Hydroponic treatment systems used aquatic plants effectively

for treatment of phosphorus. Solar aquatics systems used sunlight in coordination with

other aquatic plants and animals to treat phosphorus from wastewater. Hydroponic and

solar aquatic systems were shown to be effective wastewater treatment systems,

especially for treatment of nutrients. Other innovative natural treatment systems were

also tested to be effective for phosphorus removal. However, these treatment systems

were laboratory based studies and there were no evidence of practical applications of

food web system or periphyton – fish system.

Table 3-7. Comparative phosphorus removal at municipal wastewater in various ecological water treatment technologies

Type of technology	Operating feature*	Initial P (mg/L)	Max % removal	Reference
Wetland	2630 m² constructed wetland	10.9	74	Mander and Mauring, 1997
	231 ha of natural wetland	2.5	68	Zhang et al., 2000
	1560-3120 m²	0.33	90	Cameron et al., 2003
	12-200 l tank	5.9-15.5	96	Mars et al., 2003
Hydroponic	Flow of 1-2.9 m³/d	1-5	55	Furukawa and Fujita, 1993
	10 l/min of flow	4-16	47	Vaillant et al., 2003
	19 weeks of test	7-10.3	90.6	Mant et al., 2003
	6 troughs - 22.5 l each	1.07-4.4	77	Rababah and Ashbolt, 2000
Solar aquatic	465 m² of greenhouse	43	84.8	Teal and Peterson, 1993
	1200 gallons/d	28	65.2	Spencer, 1990
Food web system	Phytoplankton and Daphnia used	2.3-3.8	56	Kim et al., 2003b
Periphyton–fish system	Algae and fish used	0.3-1.2	82	Rectenwald and Drenner, 2000

* key design features

3.4.7 Applications for small-scale phosphorus treatment

Physical chemical processes were shown previously to be effective technology for

phosphorus removal. The use of waste materials can provide a very cost effective means

of phosphorus removal. Table 3-8 summarizes the key features for selecting any physical

chemical treatment technologies. Adsorption as a process uses materials more efficiently

than chemical precipitation. Therefore, adsorption as a treatment option for small-scale

Table 3-8. Schematic framework for issues in major physical chemical phosphorus

removal processes

Process	Max % removal	Operational issues	Applications
Coagulation	100	- Low initial cost - Coagulant required on-site - Sludge disposal concerns - Residual chemical concerns	- Wastewater having high particulate phosphorus. - Places, where low cost coagulants are available
Adsorption	100	- Easy to operate - Low maintenance costs - Material used more efficiently than coagulants - Space efficient	- Treatment of secondary effluent - Places, where low cost adsorbents are available
Membrane	90	- High initial cost - Simple to operate - Backwashing and fouling concerns - Can be successful with other treatment process	- Wastewater having large particulate phosphorus - Treatment of secondary effluent - Places need reuse of water
Wetland	90	- Success depends on loading rate and detention time. - Use of effective adsorbents in constructed wetland can increase efficiency - Wildlife considerations are needed	- Availability of existing wetland - Availability of land area is important for natural wetland
Hydroponic system	90.6	- Hydraulic loading rate should be consistent with plant uptake - Reduces sludge disposal concerns	- Availability of land area - Suitable where water is scarce and reuse is essential
Solar aquatics	84.8	- Stable and resilient system that can adapt to effluent changes - Vulnerable to changes in hydraulic loading - Reduces sludge disposal concerns	- Can be applied where greenhouses are available - Suitable where sunlight is available for longer hours

applications can reduce the hazard and sophistication of handling waste. The use of adsorbents after recirculating biofilter can also provide some cost effective advantage for on-site wastewater systems. Small municipalities can upgrade their existing treatment facilities with addition of suitable physical chemical treatment alternatives. However, selection of low cost locally available material is needed for the successful application of these technologies. Membrane technologies require further research for development as a cost effective phosphorus treatment alternative. Ecological wastewater treatment technologies were also shown to be effective in recent years, especially for rural or small-scale wastewater. These technologies can provide sustainability as part of technological options. However, most ecological treatment technologies require large land area and are often dependent on hydraulic detention time.

3.5 Summary

Small-scale wastewater systems are typically small wastewater generated from municipal or aquacultural facilities. The term 'small' in the context of this thesis is referred to as wastewater flow rate of $0.045 \ m^3/s$. In the Canadian context, small-scale wastewater is shown to contribute considerable amounts of phosphorus discharge in surface water. Physical chemical phosphorus removal technologies have been so far predominantly used as coagulation and adsorption processes. The types of material play a major part in the physical chemical phosphorus removal behaviour. Ecological and membrane based phosphorus removal technologies are also being used in recent years. Discussions on relative advantages and disadvantages among various phosphorus removal technologies revealed that adsorption can provide an appropriate technological solution in context to

small-scale wastewater solutions. Use of waste materials can provide a low cost solution

for treating small-scale wastewater.

4.0 MATERIALS AND METHODS

4.1 Introduction

The objective of this chapter was to describe the experimental methods used in various types of experiments conducted during the course of the project. Static batch and fixed bed column tests were conducted for adsorption of phosphorus on alum sludge. Jar tests were conducted for bench scale representation of coagulation. This chapter included experimental techniques used in characterizing surfaces, including infrared and raman spectroscopy, measurement of specific surface area, X-ray diffraction and scanning electron microscopy. The experimental methods used in leaching tests used for waste disposal practices were also described.

4.2 Materials

4.2.1 Alum sludge

Alum sludge is a waste material generated during the coagulation/sedimentation process in a drinking water treatment plant. Interestingly, it has been shown that adsorption is the main mechanism for P-removal during alum coagulation. Alum sludge that is generated from drinking water treatment contains precipitated alum hydroxides and the contaminants that are specific to the raw water chemistry. In this research, alum sludge was collected from the Lake Major Water Treatment Plant, Halifax Regional Municipality, Canada. The key treatment processes in this plant included coagulation, flocculation and sedimentation followed by filtration and disinfection. The plant used lime for pH control and alum as a coagulant for removing organic matter and metallic contaminants. This alum sludge collected from the sedimentation tank was primarily

composed of Al, Fe and Mn (Table 4-1). Three different types of dried alum sludge were used in this research.

Table 4-1. Inorganic parameters in alum sludge from Lake Major Water Treatment Plant

Constituent	Units	Weight
Aluminum	mg /kg	100,000
Iron	mg /kg	6800
Manganese	mg /kg	1300
Chromium	mg /kg	99
Vanadium	mg /kg	82
Zinc	mg /kg	63
Lead	mg /kg	58
Barium	mg /kg	52
Arsenic	mg /kg	30

4.2.1.1 Oven Dried Alum Sludge

Oven dried sludge has not been reported in the literature, if at all, as a phosphorus adsorbent. Alum sludge used in this research was heated in an oven at $105^{0}C$ for 24 hours. The dried sludge was then cooled to room temperature. The sludge particles were then crushed using mortar and pestle to the equivalent size distribution of conventional commercial adsorbent granular activated carbon (d_{60} of 1.25 mm) and were stored in a dessicator (Figure 4-1).
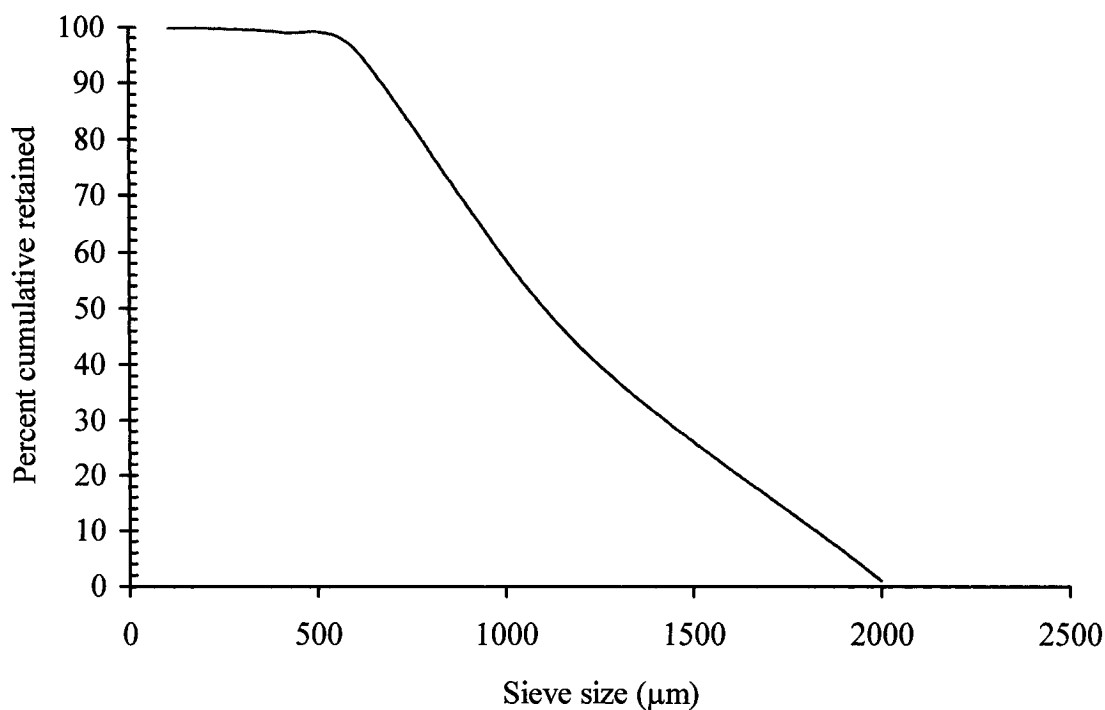
Figure 4-1. Particle size distribution of oven dried alum sludge

4.2.1.2 Air Dried Alum Sludge

Air dried sludge has been previously shown to be an effective adsorbent for phosphate

(Huang and Chiswell, 2000; Kim et al., 2003a). In this research, alum sludge was dried in

the air. The sludge particles were then crushed with mortar and pestle to produce a

particle size (d_{60}) of 1.25 mm.

4.2.1.3 Freeze Thaw Dried Alum Sludge

Freeze-thaw mechanisms are very common for drying alum sludge at water treatment

plants. In this project, freeze thaw mechanism was used to dry the sludge. As a

precautionary step, the sludge was dried in the air afterwards. A particle size of 1.25 mm

was also used for comparative purposes.

4.2.2 Blast furnace slag

Blast furnace slag is a waste material generated in steel manufacturing. The blast furnace slag used in this experiment was collected from Sydney Steel Corporation, Nova Scotia. The slag was primarily composed of CaO (40.4%-39.5%), SiO_2 (28.3%-32.0%) and Al_2O_3 (11.2%-11.7%) (SYSCO, 2004). The particle size of blast furnace slag used during this research had a d_{60} of 1.25 mm.

4.2.3 Cement kiln dust

Cement kiln dust is a fine material that is carried by hot gasses in a cement kiln and collected by a filter system during the production of cement. Studies showed that cement kiln dust can be an effective adsorbent for other types of contaminants (Fadali et al., 2004; Nassar et al., 2002; Mikhail et al., 2002; Smith and Campbell, 2000). Cement kiln dust for this research was collected from Lafarge Cement Plants, Brookfield, Nova Scotia. Typical cement kiln dust was formed with CaO (40.31%) and SiO_2 (13.46%) (Baghdadi et al., 1995) and the particles were dusty and powdery in form. The particle size was less than 0.1 mm, which was determined through a sieve analysis.

4.2.4 Limestone

Limestone used in this research was collected from local stores. Regionally available these limestone was composed of $CaCO_3$ (96%) and MgO and SiO_2 were less than 2% (Nova Scotia Department of Natural Resources, 1993). The particles size of limestone was selected to be 1.25 mm through a sieve analysis.

4.2.5 Granular activated carbon

Granular activated carbon is one of the most widely used adsorbent for organic, metallic and inorganic contaminants in water. It was used in this research as a reference by which to compare adsorption other inorganic adsorbents. The granular activated carbon was coal based and supplied by Nichem Carbon Company. The particle size used in this research (d_{60}) was 1.25 mm.

4.2.6 Bone char

Bone char is a carbon based modified natural material. It has been proved to be a very useful adsorbent for various types of metals (Cheung et al., 2001; Cheung et al., 2002). Bone char was used in this research to compare the performance of alum sludge. The available particle size was <0.45 mm, as supplied by Tate and Lyle North America.

4.2.7 Wastewater

Deionized water was spiked with KH_2PO_4 to prepare a phosphorus solution of 2.5 mg/L. The concentration of 2.5 mg/L was chosen as secondary municipal effluents typically have a phosphorus concentration of 2.5-3 mg/L (Environment Canada, 2001). High phosphorus concentrations were prepared similarly to 10 mg/L. Orthophosphates were chosen as it is the key species of phosphorus in most wastewaters (Mann, 1996). The phosphorus concentration was chosen as a typical phosphorus concentration in many wastewaters. Small-scale wastewaters were collected from secondary municipal effluent from Millcove Water Pollution Control Plant, Nova Scotia, Canada, biofiltration effluent

from Municipality of Lunenburg, Nova Scotia, Canada and bench scale experiments

conducted at Dalhousie University, Canada, and an aquaculture processor in Atlantic

Canada. These wastewaters contain orthophosphate phosphorus concentration of 1.3

mg/L to 6.6 mg/L and total phosphorus concentration of 2.0 mg/L to 7.2 mg/L (Table 4-

2).

Table 4-2. Effluent wastewater characteristics from various small-scale wastewaters

Characteristics	Unit	Secondary municipal	Plant scale biofiltration	Bench scale biofiltration	Aquaculture process
pH		7.23	6.16-6.50	5.53-7.29	6.48
BOD_5	mg/L	33.6	126	7.5-39.3	55.2
Aluminum	mg/L	0.19	0.082	0.02-0.13	0.001
Orthophosphate – P	mg/L	3.0	5.2	3.4-6.6	1.3
Total Phosphorus	mg/L	3.8	7.2	4.5-6.8	2.0

4.3 Bench Scale Phosphorus Removal Tests

Bench scale tests were conducted during the project. Tests include adsorption and

coagulation based tests, characterizing alum sludge surfaces and leachability tests in both

land based and water based disposal systems.

4.3.1 Batch adsorption tests

Five Erlenmeyer flasks were used for each material with 250 mL of wastewater.

Materials were used in the concentrations of 0 g/L, 4 g/L, 8 g/L, 12 g/L and 16 g/L. For

experiments conducted with an initial phosphorus concentrations of 10 mg/L, alum

sludge was used in concentrations of 0 g/L, 8 g/L, 26 g/L, 24 g/L and 32 g/L.

Temperature was controlled at $21.98 \pm 1.15°C$ and any mechanical shaking was avoided.

Preliminary experiments showed that adsorption equilibrium is reached in 3 to 7 days

(Figure 4-2). Equilibrium was assumed when changes in concentration was less than 0.02

mg/L. However, batch adsorption experiments were conducted for 12 days to ensure

adsorption equilibrium. Samples were collected from the flasks and after 12 days tested

for pH, temperature and total orthophosphate phosphorus. Phosphorus that was lost from

the solution was assumed to be adsorbed onto the adsorbents.
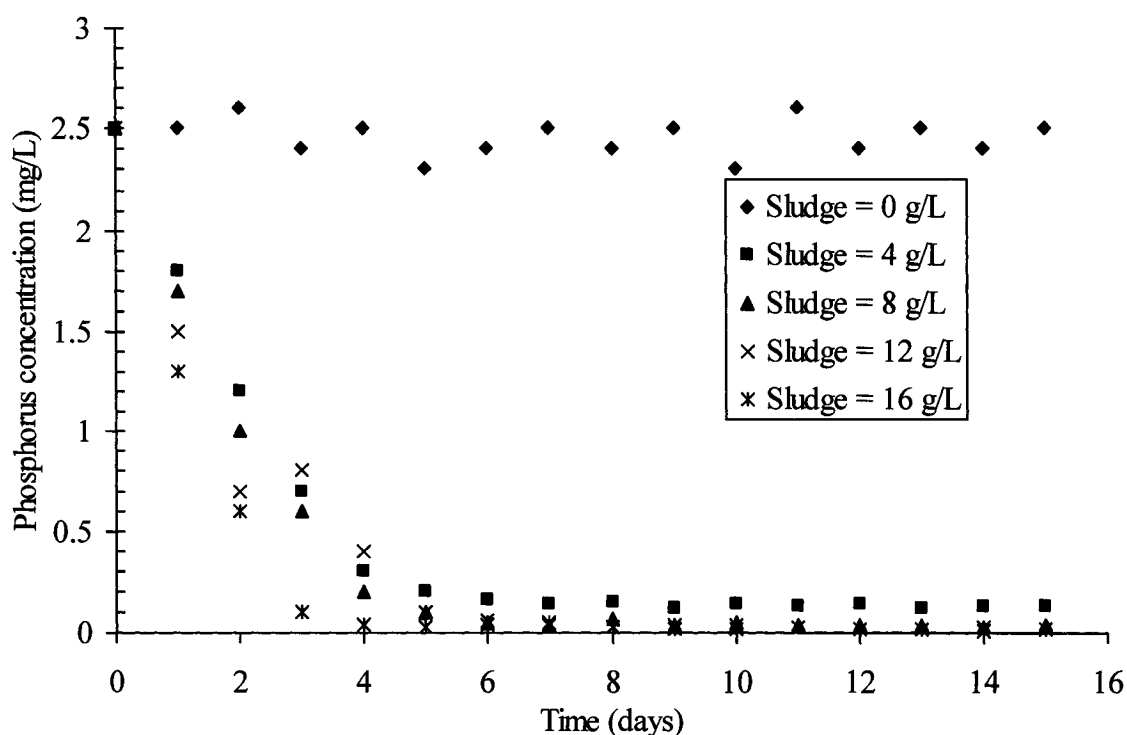
Figure 4-2. Changes in phosphorus concentration in various days of batch tests

Data obtained from batch tests conducted on deionized water were fitted to both

Freundlich and Langmuir adsorption isotherm equations.

4.3.1.1 Freundlich Equation

The Freundlich adsorption isotherm equation is normally expressed as:

$$Q = K_d C_e^{\frac{1}{n}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4\text{-}1$$

In equation (4-1), Q is adsorption density of the adsorbent (mg P/g of adsorbent in this study), C_e is the solution phosphorus concentration at equilibrium, and K_d and n are material characteristics and considered constant for each adsorbent and adsorbate group. The constant K_d is considered as the adsorption density for an unit value of C_e. Thus K_d is often used to understand the adsorption capacity of various materials. Equation (4-1) can also be written as:

$$\log Q = \log K_d + \frac{1}{n}\log C_e \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4\text{-}2$$

A linear plot of log Q and log C_e provides the value for K_d and n in the form of intercept and slope.

4.3.1.2 Langmuir Equation

The Langmuir adsorption isotherm equation is expressed as:

$$Q = \frac{Q_{max} K C_e}{K C_e + 1} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4\text{-}3$$

In equation (4-3) Q_{max} and K are materials characteristic and constants for each adsorbent and adsorbate group. Q_{max} is the maximum adsorption density. The constant K is related to binding energy. The values of Q_{max} and K are computed from the slopes and intercepts generated from a linear plot of C_e/Q and C_e. The linearized form of equation (4-3) can be written as:

$$\frac{C_e}{Q} = \frac{1}{Q_{max}}C_e + \frac{1}{K}\frac{1}{Q_{max}} \quad\dotfill\quad 4\text{-}4$$

4.3.2 Fixed bed column tests

Rapid small-scale laboratory based experiments are designed to simulate the adsorption

behavior in large-scale adsorbers. RSSCT uses empty bed contact time (EBCT) and

hydraulic loading to describe the adsorption process (Crittenden et al., 1986). It uses

dimensionless numbers to correlate full-scale and RSSCT parameters. The use of RSSCT

was later adapted in ASTM standard (ASTM, 2000). Rapid small-scale column tests

(RSSCT) were used for fixed bed column tests. The experiment was conducted with a

fixed column, having 20 cm in length and 2.5 cm in diameter. The column was filled with

adsorbent at a porosity of 0.6. Wastewater was passed through the column in an upflow

mode (Figure 4-3). Different flows were used in the experiments for different types of

wastewater, as the results presented in a dimensionless form was expected to incorporate

the differences involved due to flow. This was done for detailed investigation for many of

the column tests up to the breakthrough time.
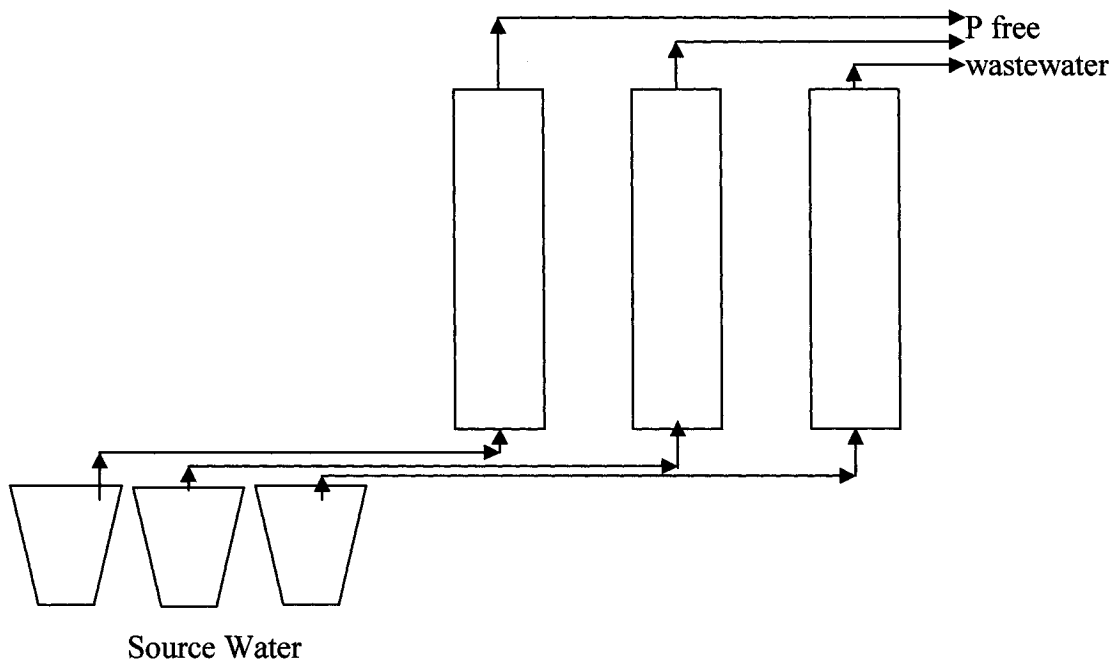
Figure 4-3. Experimental setup for RSSCT experiments

4.3.3 Coagulation based tests

Jar tests were used in the laboratory for coagulation process (Figure 4-4). Six jars were

subjected to mechanical rotation of a certain speed. Jar tests were conducted based on

USEPA guideline for enhanced coagulation (USEPA, 1999b). One litre of raw water was

used during the experiment. High-speed mixes were used for 1 minutes and a slow mix of

30 minutes were used for flocculation and 60 minutes for sedimentation. Once the

sedimentation time was over, the samples were collected from the sampling port just

above a typical sludge layer. Sludge was assumed to be the bottom 100 ml after pouring

the supernatant. These samples were later used for chemical analysis. Total phosphorus

(TP), orthophosphate-phosphorus (OP) and particulate phosphorus (PP) were the

different types of phosphorus tested.

Port for
taking
samples

Jars
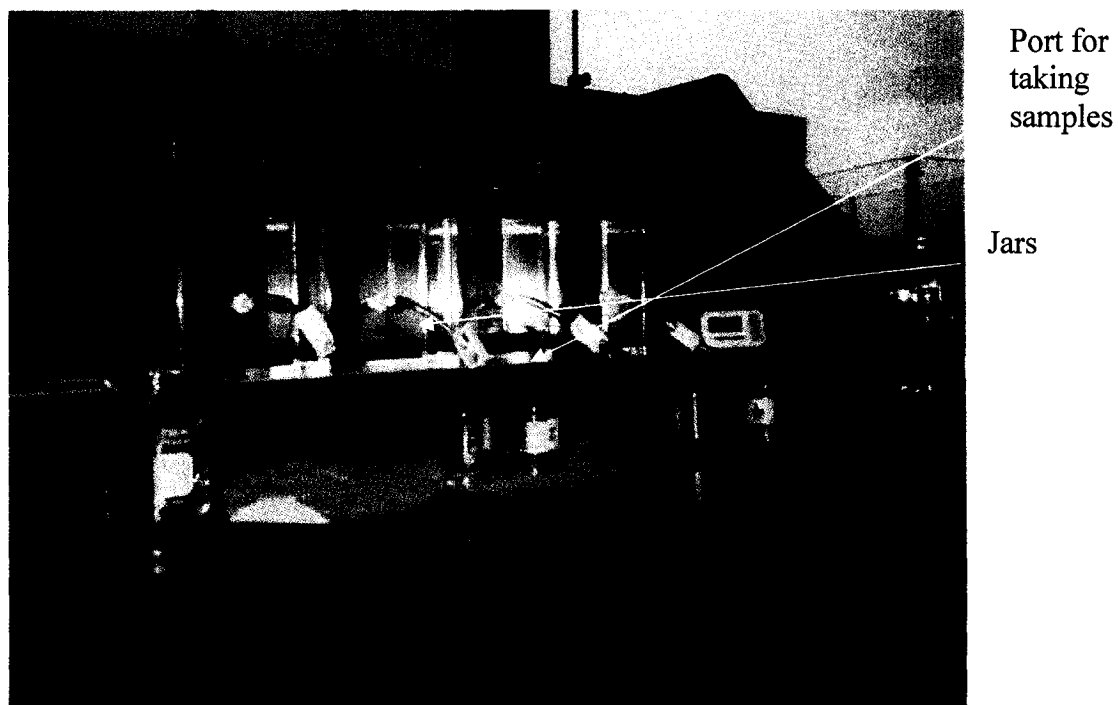
Figure 4-4. Jar test apparatus

4.4 Tests for Characterizing Oven Dried Alum Sludge

4.4.1 IR spectroscopy

The samples for infrared spectra (Bruker Vector FT-IR spectrometers) were prepared

with methylene chloride (CH_2Cl_2) mulls on CsI plates using. Vibrational spectra were

reported in wavelengths (cm^{-1}) against ranked infrared absorption, where value of

wavelengths at peak corresponds to the characteristics of active groups present on the

surface of the material.

4.4.2 Ramans spectroscopy

Raman spectra were collected on powdered samples, sealed in glass capillaries under dry nitrogen, using a Bruker RFS 100 FT-Raman spectrometer. The spectra were reported in wavelengths (cm^{-1}) against ranked raman intensities, where a value of wavelengths at peak corresponds to the active groups on the material surface.

4.4.3 X-ray diffraction

X-Ray powder diffraction patterns of oven dried alum sludge were obtained from gently pressed specimens of random powder particles that are less than 0.45 μm. Powder X-ray diffraction data were collected from 10 to 60° 2δ with a Nicolet X-ray powder diffractometer (graphite monoachromatized Cu KR radiation, 0.05° 2δ step size, and 2-s count time per steps).

4.4.4 Specific surface area

Specific surface area was measured using the procedure suggested by American Society of Agronomy for soils (Klute, 1986). The sample was pre-treated with H_2O_2 to remove organic matter, and saturated with calcium ($CaCl_2$) and then dried with air. The sample was also heated for 600^0C for 2 hours. A 0.70 g of oven dried alum sludge was taken in aluminum can and dried with P_2O_5 in a vacuum desiccator. 3 mL of reagent-grade ethylene glycol monoethyl ether (EGME) was mixed with the sample to make slurry. The slurry was placed with $CaCl_2$-EGME solvate within a culture chamber in a vacuum desicator. The sample weight was measured once in every 2 hours until constant weight

reached. The weights were used to calculate the specific surface area. Six samples were used to get an average value for specific surface area.

4.4.5 Scanning electron microscopy

Scanning electron microscopy (SEM) was conducted to learn the surface roughness of the alum sludge samples. Secondary and back-scattered electron images were taken at various magnifications. Samples were ground to fine particles for getting better SEM pictures.

4.5 Leaching Tests

4.5.1 Toxicity characteristics leaching procedure

Toxicity characteristics leaching procedure tests were conducted based on procedure suggested by USEPA method 1311 (USEPA 1992). Extraction fluid was prepared by using both glacial acetic acid and sodium hydroxide in the stated proportion. Alum sludge was mixed with extraction in the standard proportion (1:20 solid to extraction fluid) and rotated for 18 hours. The generated solution was then filtered through 0.45 micron filter to get the leachate. The leachate was then tested for aluminum and manganese.

4.5.2 Surface water leaching

Surface water leaching experiments were conducted based on the procedure used by (George et al., 1995). Residuals containing 6 grams of solids were used in 250 mL of water collected from Pockwock Lake, Halifax, Canada. These mixtures of sludge to lake water were mixed on a shaker table for one hour and then kept in an isolated environment

for 30 days for these mixtures to leach. After 30 days, this lake water was tested for soluble aluminum and phosphorus.

4.6 Analytical Measurements

Analytical techniques were used from standard methods for water analysis (APHA-AWWA-WEF, 1995). A spectrophotometer (DR – 4000, Hach Co., Coveland Co.) was used for measurement of orthophosphate (OP) at a wavelength of 890 nm. Total phosphorus (TP) was measured after digesting samples with potassium persulfate at 150^0C for 30 minutes. The samples were then cooled down to room temperature. The samples were then tested for total phosphorus using a spectrophotometer at 890 nm. Particulate phosphorus (PP) was measured by deducting soluble phosphorus from total phosphorus as mentioned by Standard Methods (APHA-AWWA-WEF, 1995). Total soluble phosphorus was measured as total phosphorus after filtering the samples through 0.45 μm. Temperature and pH were measured using a pH probe (model 230A, Orion), which was calibrated on a daily basis. A spectrophotometer (DR – 4000, Hach Co., Coveland Co.) was used for measurement of aluminum using aluminon method. BOD_5 was measured using a DO probe (Sension 378, Hach Co., Coveland Co.) for both sample collection day and after five days. Turbidity was measured by a portable turbidimeter (HACH 2100P). Total suspended solids of the sludge were measured using standard procedure 2540 D from Standard Methods (APHA AWWA WEF 1995).

4.7 Quality Control and Statistical Analysis

Wastewater and various samples were preserved in the freezer so that BOD values do not alter much. The samples were measured immediately after collection. In odd circumstances, these samples were collected in a closed environment in the freeze. For samples that are affected by air and water vapour were collected in a desiccator. In cases of unreasonable results, the samples were tested more than three times and the averages of them were reported for better accuracy. Reproducibility of the test was conducted on each bench scale tests to understand the experimental accuracy in each setup. Method detection limit (MDL) was measured as part of understanding the accuracy of the analytical measurements. MDL for a sample of 2.5 mg/L of phosphorus concentration and with a degree of freedom 35 was observed to be 0.056 mg/L. It implied that the concentrations values of 0.056 mg/L or higher was measured and reported with 99% confidence. The tests conducted for measurement of phosphorus showed an average concentration of 2.508 mg/L (standard deviation 0.02086 mg/L) for a nominal phosphorus concentration of 2.5 mg/L (Table 4-3), contributed to 0.34% error. Similarly, for a nominal phosphorus concentration of 10 mg/L, the average phosphorus concentration observed were 10.011 mg/L (standard deviation 0.02748 mg/L) that contributed to 0.11% error.

Tests were designed in an organized manner so that it could produce effective results with the least number of experiments. Key factors that affect the experimental output were set with factorial design prior to conducting experiments. Results from the experiments were analyzed using one-way and two-way analysis of variance (ANOVA)

tests. Unless otherwise noted, the level of significance for these tests was 5%. There were paired and independent t tests conducted based on the relevant data.

Table 4-3. Variability of testing procedure

	Nominal P = 2.5 mg/L					Nominal P = 10 mg/L	
Tested P (mg/L)	2.49	2.52	2.50	2.48	2.53	10.04	10.01
	2.51	2.51	2.52	2.50	2.49	9.97	10.06
	2.51	2.50	2.55	2.45	2.52	10.01	10.03
	2.52	2.51	2.50	2.53	2.48	10.02	10.01
	2.53	2.48	2.51	2.50	2.48	9.98	10.04
	2.51	2.51	2.51	2.50	2.52	10.04	9.99
	2.55	2.51	2.50	2.51	2.48	9.99	9.97
Avg. P (mg/L)	2.508					10.011	
% Error	0.34					0.11	
Standard Deviation (mg/L)	0.02086					0.02748	

5.0 PHOSPHORUS ADSORPTION IN NATURAL AND INDUSTRIAL WASTE MATERIALS

5.1 Introduction

There is a general lack of technologies for small municipal and/or decentralized wastewater systems (Chapter 3). A potential concern with previous work is the unavailability of relative performance to other value added materials. Thus the need for comparative studies under controlled conditions between adsorbents is great, as there is little, if any, comparing relative capacity and performance.

The objective of this chapter was to compare phosphorus adsorption behaviour of second generation products and natural materials under similar test conditions. In particular, orthophosphate removal in both deionized water and secondary municipal effluent were tested.

5.2 Experimental Approach and Setup

Batch adsorption experiments were conducted for the adsorbents mentioned in Chapter 4. The experiments were conducted in two different phases. In the first phase, deionized water spiked with orthophosphate concentration was used as raw water. In the second phase of experiment, adsorbent concentration of 16 g/L was used in batch adsorption experiments with effluent from a secondary municipal wastewater treatment plant mentioned in Chapter 4. Deionized water was spiked with KH_2PO_4 to prepare a phosphorus solution of 2.5 mg/L. Batch tests conducted on oven dried alum sludge (ODS), granular activated carbon (GAC), blast furnace slag (BFS) and limestone were

repeated three times to show the repeatability of these test results for each concentrations

of adsorbent. For other materials (freeze thaw dried sludge (FDS), air dried sludge

(ADS), cement kiln dust (CKD) and bone char), tests were repeated three times for

adsorbent concentrations of 0 and 16 g/L only.

The repeatability of the experimental results were measured by conducting paired t tests

for ODS, GAC, BFS and limestone, taking two set of tests (replicated) together at a time.

The level of significance for these paired t tests at $\alpha = 0.05$. For other materials, repeated

tests results were presented using an average value and standard deviation. pH results for

the experiments using deionized water were evaluated with a t-test at $\alpha = 0.05$ to

determine whether there was a significant change between the initial pH and an average

of the final pH for each of the materials.

5.3 Results and Discussions

5.3.1 Phosphate adsorption from deionized water

The results from phosphorus adsorption experiments conducted in deionized water

showed that most of the materials tested were capable of removing phosphorus. Paired t

tests conducted on some materials showed that the repeated test results were statistically

indifferent. The average phosphorus concentration and standard deviation for bone char,

FDS, ADS and CKD for the repeated tests also showed reproducible results (Table 5-1).

Among the materials, bone char, dried alum sludge (oven, air and freeze/thaw), cement

kiln dust and blast furnace slag were the most efficient orthophosphate adsorbent

materials (Figure 5-1). Limestone was the only material that showed very poor

phosphorus removal (less than 20% removal). The phosphorus removal achieved with

blast furnace slag and alum sludge was consistent with previous studies (Sakadevan and

Bavor, 1998, Kim et al., 2003a). However, the adsorption density for alum sludge was

observed to be much lower than previous studies probably due to differences in alum

sludge composition (Kim et al., 2003a). In this experiment, limestone did not show

similar phosphorus removal behaviour to previous studies (Johansson, 1999a).

Experiments with limestone were replicated and produced identical results. It was

possible that the limestone results were specific to the commercial limestone studied.

Table 5-1. Reproducibility of effluent phosphorus concentration for ADS, FDS, CKD and
bone char

Initial adsorbent (g/L)	Values	ADS	FDS	CKD	Bone char
0	Average (mg/L)	2.633	2.633	2.68	2.67
	Standard deviation (mg/L)	0.029	0.028	0.028	0.03
16	Average (mg/L)	0.22	0.137	0.087	0.207
	Standard deviation (mg/L)	0.026	0.032	0.015	0.031
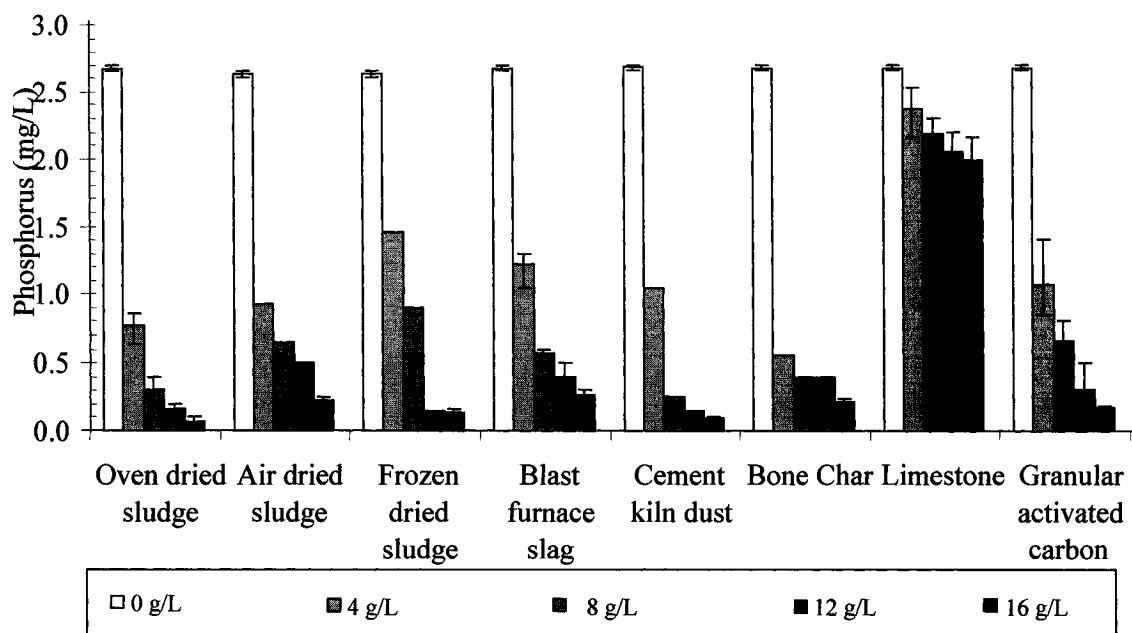
Figure 5-1. Phosphorus concentration in deionized water at an initial phosphorus

concentration of 2.5 mg/L

Solution pH at equilibrium increased for all adsorbents (Figure 5-2). Statistically, the

initial pH and an average of the final pH levels failed a t-test at $\alpha = 0.05$, indicating that

the differences in solution pH was not significant. In the batch experiments using the

three types of dried alum sludge the solution pH did not increase abruptly, and was in the

range of 6.5 to 7.5. For other materials tested, the solution pH increased and in most of

the cases it was above 8. The solution pH is particularly important in the context of

wastewater discharge into surface water. The deionized water did not have any buffering

capacity and was therefore vulnerable to pH changes from the media.
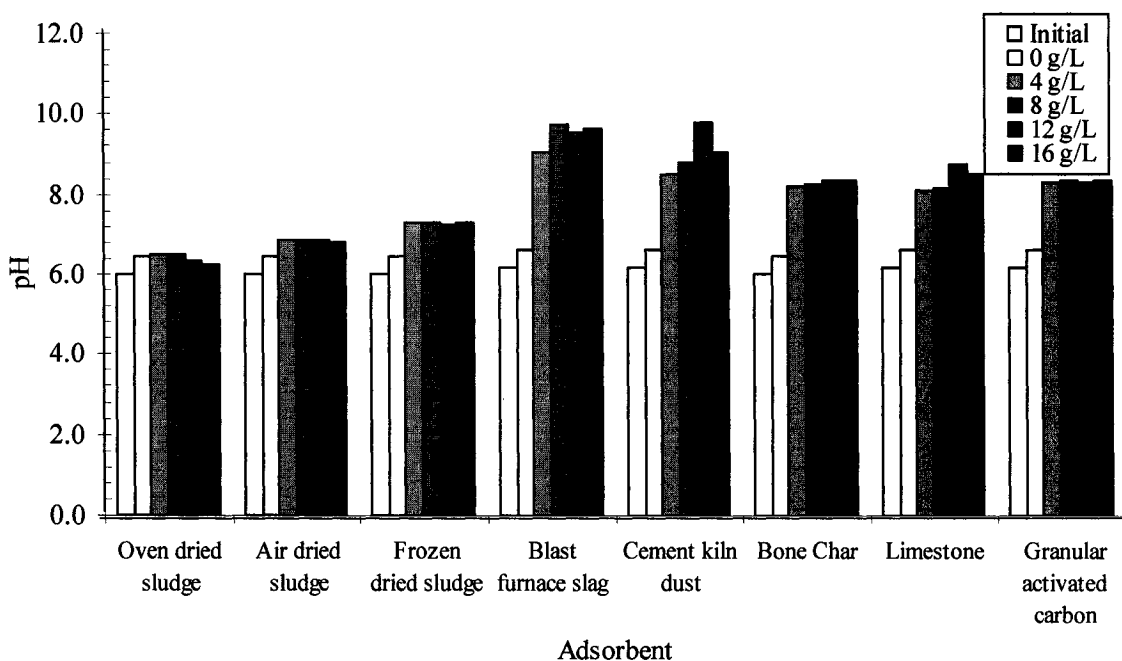
Figure 5-2. Solution pH following batch adsorption in deionized water at an initial

phosphorus concentration of 2.5 mg/L

Data obtained from these experiments were fitted into the two most commonly used

adsorption isotherm equations (Freundlich and Langmuir). GAC demonstrated an

unfavourable isotherm pattern for both Freundlich and Langmiur, whereas limestone had

a very slow increase in adsorption density with the increase in equilibrium concentration

(Figure 5-3a). Other materials showed favourable isotherm patterns (Figure 5-3b-d). All

materials fit the data reasonably well with the Freundlich isotherm (Table 5-2). Though

there were differences in the value of R^2, bone char had the largest distribution

coefficient (K_d). Among other materials, oven dried sludge had the highest value of K_d.

Bone char also had one of the lowest values of n, indicating a rapid increase in

adsorption, although many of the materials provided adequate fit to the Langmuir

isotherm equation ($R^2 = 0.8363$-0.9986). Experimental data for air dried sludge, bone

char, and granular activated carbon did not fit with the Langmuir isotherm equation (R^2 = 0.0153-0.2966). Limestone was not effective in removing phosphorus, and therefore produced negative values of Q_{max} and K. Oven dried sludge had the highest Q_{max} of 0.674 mg P g^{-1} and blast furnace slag had the lowest binding energy (K). For treatment of 1 kg of phosphorus at 0.1 mg/L of effluent phosphorus, Cement kiln dust required the least amount. Among other adsorbents, lower amount of oven and freeze thaw dried alum sludge were required than other adsorbents.

Table 5-2. Coefficients of Freundlich and Langmuir adsorption isotherms for materials tested in deionized water

Materials*	Freundlich				Langmuir		
	R^2	K_d	n	Wt (1000 kg)**	R^2	Q_{max} (mg P g^{-1})	K (L g^{-1} P)
ODS	0.9746	0.484	1.971	5.714	0.8971	0.674	2.345
ADS	0.8286	0.382	1.302	20.000	0.0970	1.787	0.284
FDS	0.7579	0.256	5.848	5.714	0.9515	0.300	8.273
BFS	0.8901	0.317	1.695	20.000	0.9019	0.593	1.145
CKD	0.9487	0.429	2.927	5.000	0.9986	0.469	6.968
Bone Char	0.8103	1.031	0.694	20.000	0.2966	-0.548	-0.810
Limestone	0.9359	0.002	0.304	1000.000	0.8363	-0.015	-0.293
GAC	0.8185	0.240	0.930	166.667	0.0153	-3.766	-0.059

* ODS = Oven dried sludge, ADS = Air dried sludge, FDS = Freeze thaw dried sludge, BFS = Blast furnace slag, CKD = Cement kiln dust & GAC = Granular activated carbon
** Wt = Amount required to treat 1 kg of phosphorus at an effluent P of 0.1 mg/L

a) Oven dried alum sludge and air dried alum sludge

b) Freeze thaw dried alum sludge and blast furnace slag
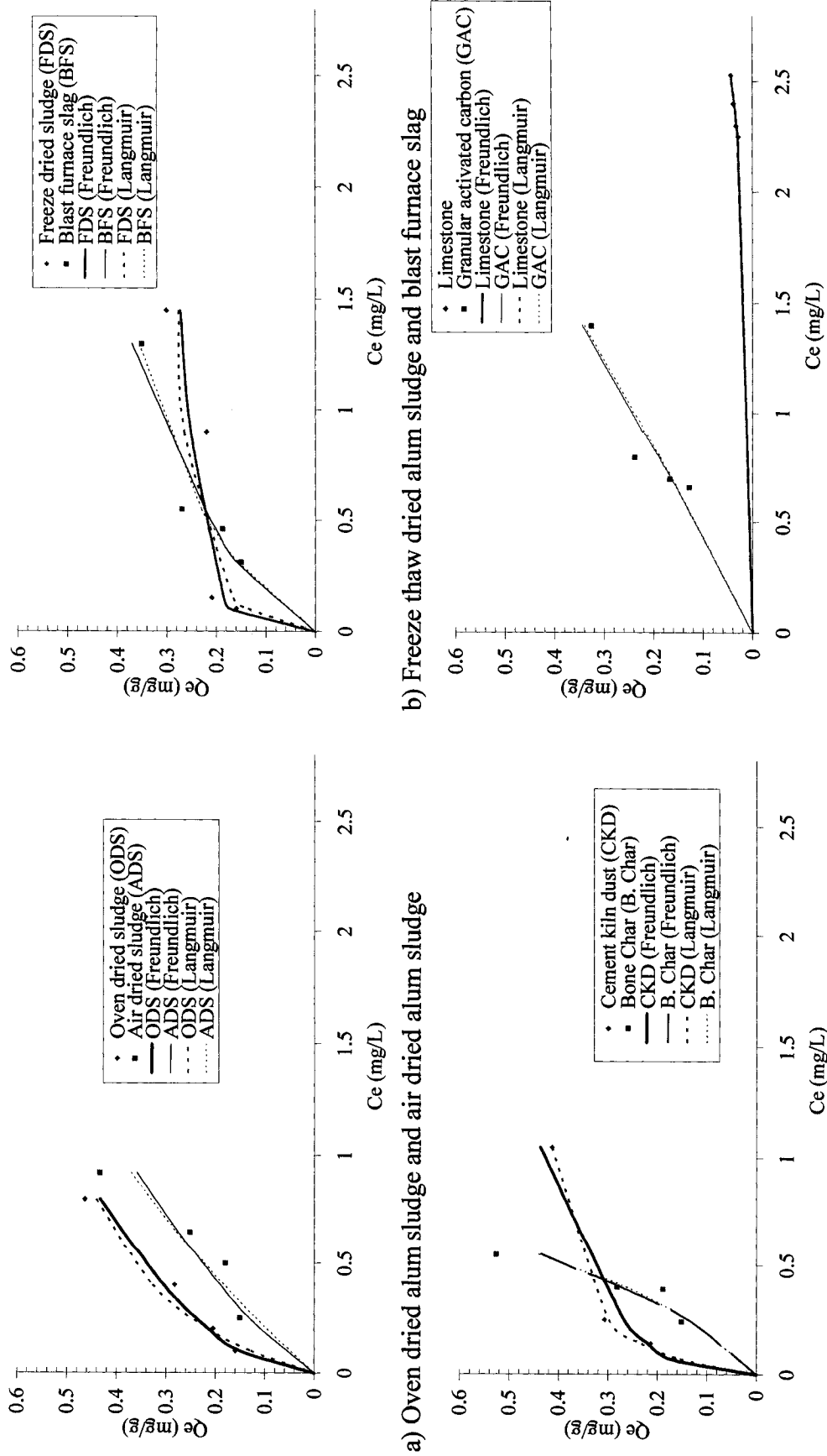
c) Cement kiln dust and bone char

d) Limestone and granular activated carbon

Figure 5-3. Adsorption isotherm for media in deionized water at an initial phosphorus concentration of 2.5 mg/L

From this experiment, bone char and oven dried sludge appeared to be the most effective adsorbent for phosphorus. Oven dried sludge provided the best fit to the Langmuir and Freundlich isotherm equations and bone char had the highest adsorption density (K_d). In general, waste materials showed competitive absorbance of phosphorus to other conventional natural adsorbents. However, several contaminants are generally present in wastewater. Therefore, experiments conducted on wastewater can provide useful information to choose suitable low cost adsorbents of phosphorus.

5.3.2 Phosphorus removal from secondary municipal wastewater effluent

Experiments conducted with secondary municipal wastewater effluent showed phosphorus adsorption of approximately 50% (or greater) for most of the materials tested (Figure 5-4). However, the three types of dried alum sludge and bone char were the most effective phosphorus adsorbents (> 80% removal). Bone char, however, has the possibility of microbial contamination during adsorption of phosphorus. The removal of orthophosphate was higher than total phosphorus. Blast furnace slag, cement kiln dust, and especially granular activated carbon were not effective in adsorbing phosphorus from wastewater. There may have been other adsorbates, which could have competed with phosphorus for adsorption sites on the blast furnace slag, cement kiln dust and granular activated carbon. Competitive species in the wastewater were not quantified for this study.
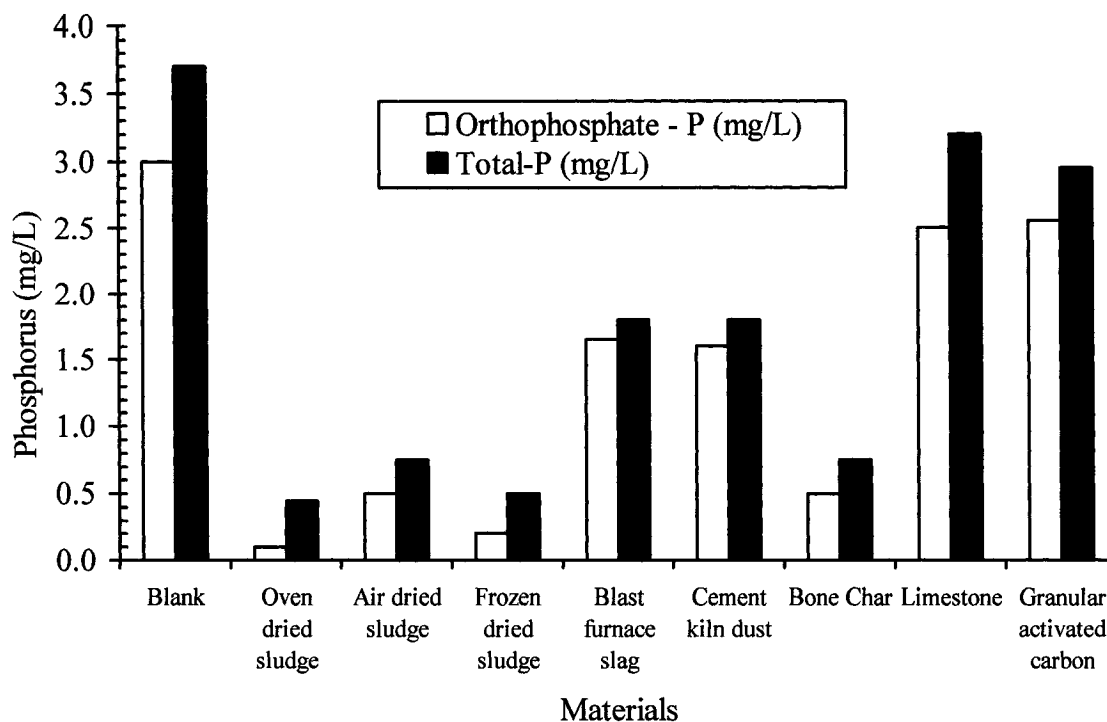
Figure 5-4. Percentage phosphorus removal for municipal effluent at an adsorbent

concentration of 16 g/L

At the end of the experiment pH levels were generally in the range 6-9, which is a

regulatory requirement for wastewater disposal to surface water (Figure 5-5). Bone char,

limestone, and granular activated carbon resulted in a solution pH remained close to 7.

Oven dried sludge and freeze thaw dried sludge resulted in a solution pH slightly less

than neutral. Experiments conducted earlier showed that oven dried alum sludge and

bone char were the most efficient adsorbents.
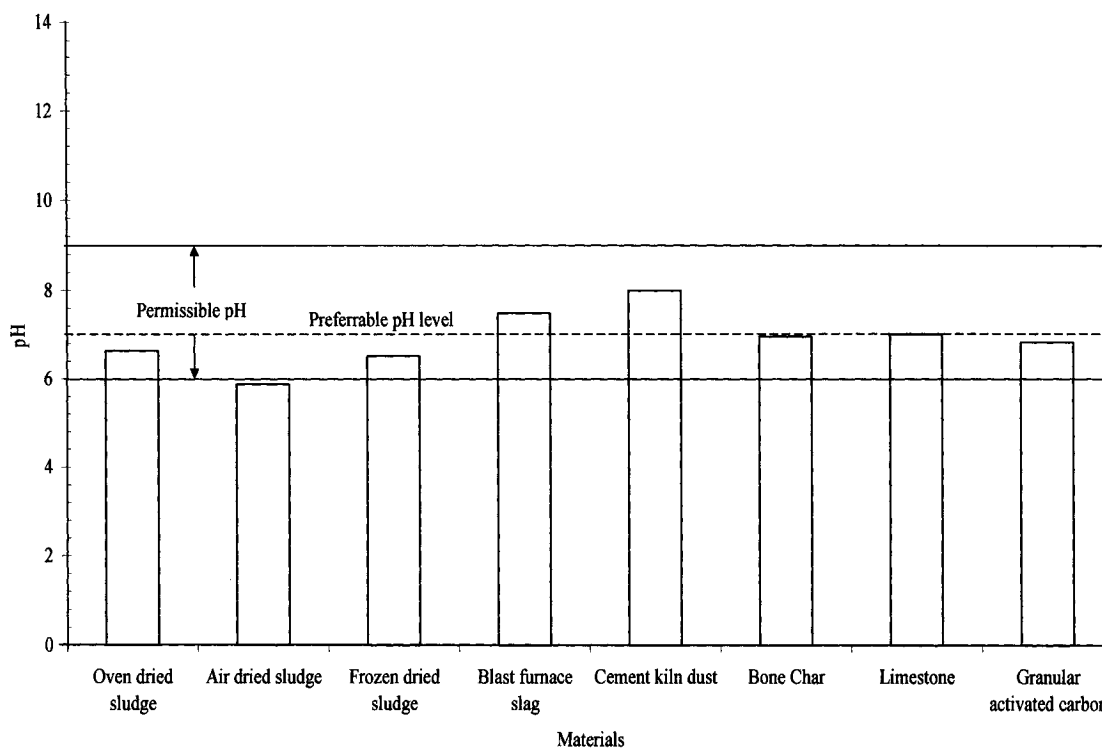
Figure 5-5. pH at the end of batch test using municipal effluent at an adsorbent concentration of 16 g/L

5.4 Conclusions

Phosphorus adsorption using natural and industrial waste materials was an effective process for phosphorus removal. Waste materials showed comparable phosphorus adsorption behaviour to natural adsorbents. Alum sludge generated at the Lake Major Water Treatment Plant, adsorbed phosphorus efficiently in both deionized water and secondary municipal effluent. The Freundlich isotherm effectively described the partitioning of phosphorus in solid and liquid phase. The Langmuir isotherm was also effective in predicting partitioning for some materials. Oven dried alum sludge was reused to ensure efficient phosphorus removal in wastewater. The study also revealed that

pH in alum sludge treated effluent can be reasonable for disposal into surface water. This study demonstrated the adsorption capacity of natural and industrial materials. However, in the following chapters, only oven dried alum sludge is used to understand the adsorption kinetics in detail.

6.0 ADSORPTION KINETICS OF OVEN DRIED ALUM SLUDGE: BATCH ADSORPTION

6.1 Introduction

Kinetic studies are important parts of adsorption research, as it helps to optimize

adsorption performance. Batch adsorption tests were useful to estimate the adsorption

density or adsorption capacity of a certain adsorbent and evaluate the effect of various

parameters on the adsorption density, as shown in Chapter 5. The objectives of this

chapter were to evaluate the effect of operating parameters (pH, initial phosphorus and

particle size) on the adsorption density and effluent phosphorus concentrations. This

chapter also examined the adsorption capability of oven dried alum sludge on various

small-scale wastewaters.

6.2 Experimental Procedure

Batch experimental setup was designed as described in Chapter 4. Oven dried alum

sludge was used in the experiments tested, as it was found to be suitable in Chapter 5.

Tests on deionized water spiked with orthophosphate concentrations were conducted to

evaluate the effect of varying pH, initial phosphorus concentration and particle size. The

three pHs used were 3, 5 and 7. pH was controlled using HCl and NaOH. The initial

phosphorus concentrations were chosen as 2.5 mg/L of phosphorus as representative of

low phosphorus concentration and 10 mg/L of phosphorus as representative of high

phosphorus concentration. The three particle sizes used were 250 μm, 425 μm and 1180

μm. These experiments were repeated. Apart from single adsorbate experiments

conducted on deionized water, various types of small-scale wastewater (mentioned at

Chapter 4) were used to evaluate the phosphorus adsorption behaviour in treatment of these wastewaters. Reproducibility of the batch test procedure was determined using six set of data for samples at five different adsorbent concentrations. The adsorbent concentrations tested were 0 g/L, 4 g/L, 8 g/L, 12 g/L and 16 g/L. The influent pH used was 5.5. Environmental conditions were set identical.

Statistical analysis was conducted using two-way ANOVA on phosphorus concentration obtained at variable pH and oven dried alum sludge concentration and also on phosphorus concentration obtained at variable particle size and alum sludge concentration. As only two different initial phosphorus concentrations were used, ANOVA was not conducted on variability of initial phosphorus concentrations. Experimental results from repetitive experiments were also used in ANOVA.

6.3 Results and Discussions

6.3.1 Reproducibility

As showed in Figure 6-1, the experimental setup appeared to produce reproducible results. Standard deviations ranged from 0.8% to 2.98% for an average phosphorus removal of 92%-98%. It was indicative that if the experimental setup and procedures were identical as used in this project, it would produce similar results. Several experiments were also repeated. See Appendix A for detail results.
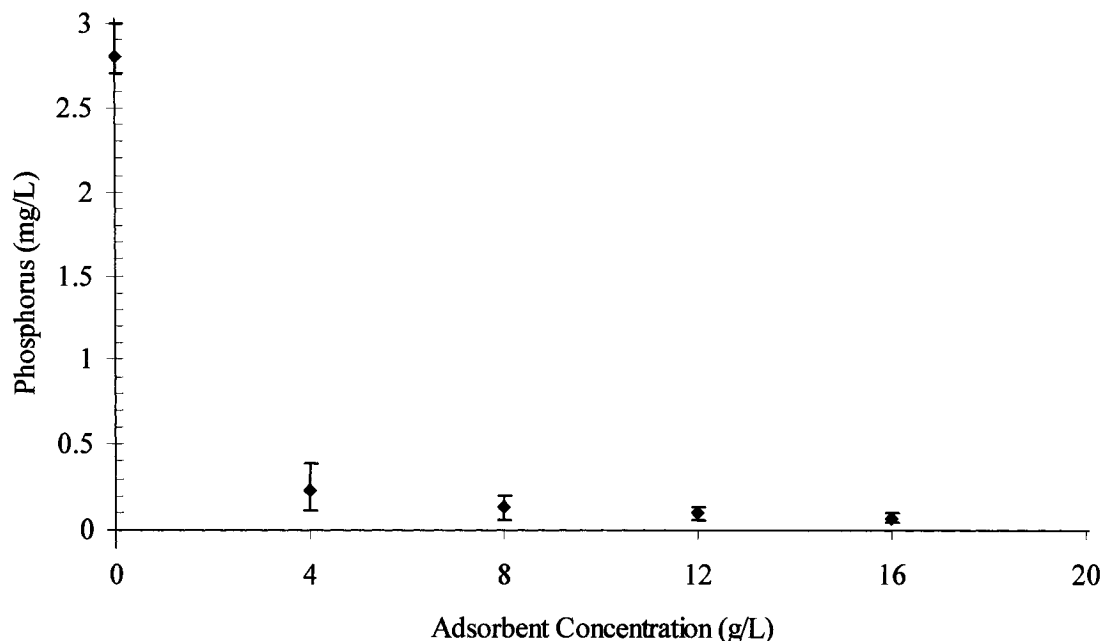
Figure 6-1. Variability of phosphorus removal with repetitive batch tests at 2.5 mg/L P at 5% level of significance

6.3.2 Effect of pH

pH had little affect on the adsorption density (Figure 6-2). However, solution pH of 5

appeared to produce maximum adsorption density in many of the experimental results.

Studies conducted by previous researchers on air dried alum sludge also did not observe

considerable effect of pH on the phosphorus adsorption behaviour within the pH levels

tested in this study (Kim et al., 2003a). For fine particles (250 μm), a solution pH of 7

appeared to produce the largest adsorption density for high initial phosphorus

concentration. The removals of phosphorus on oven dried alum sludge for all the pHs

were more than 50 %, with the majority more than 90%. pH 5 was found to consistently

produce the maximum phosphorus removal. Effluent phosphorus concentrations were
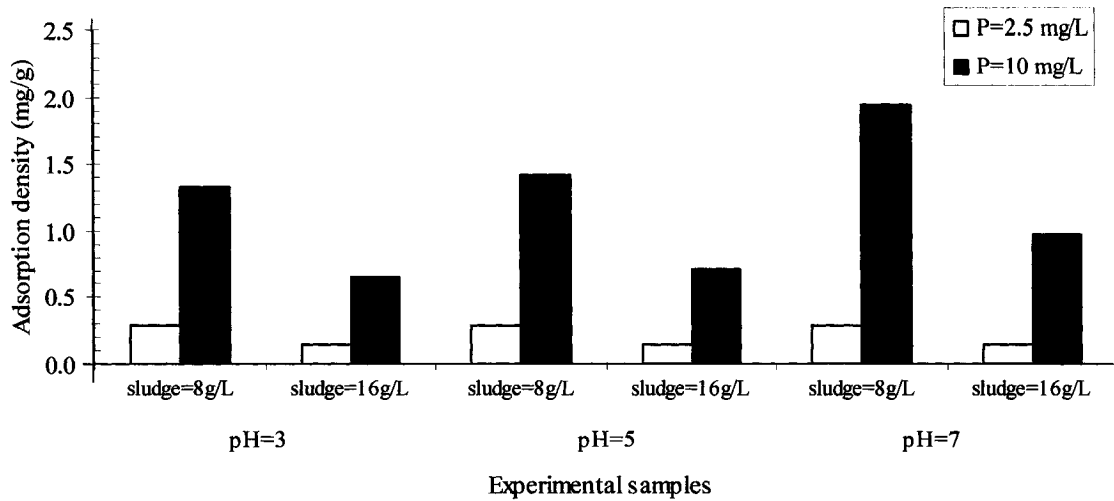
a) particle size =250 μm
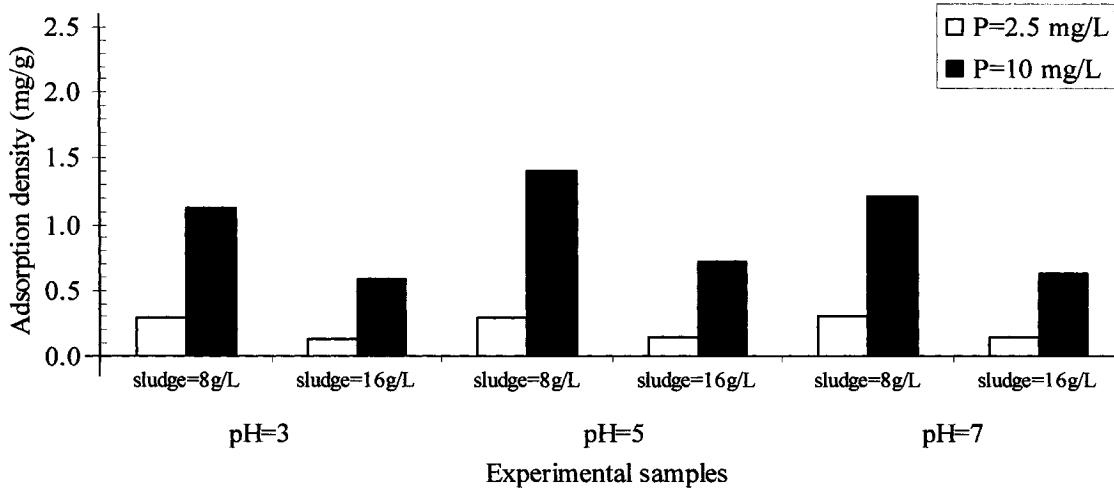
b) particle size =425 μm
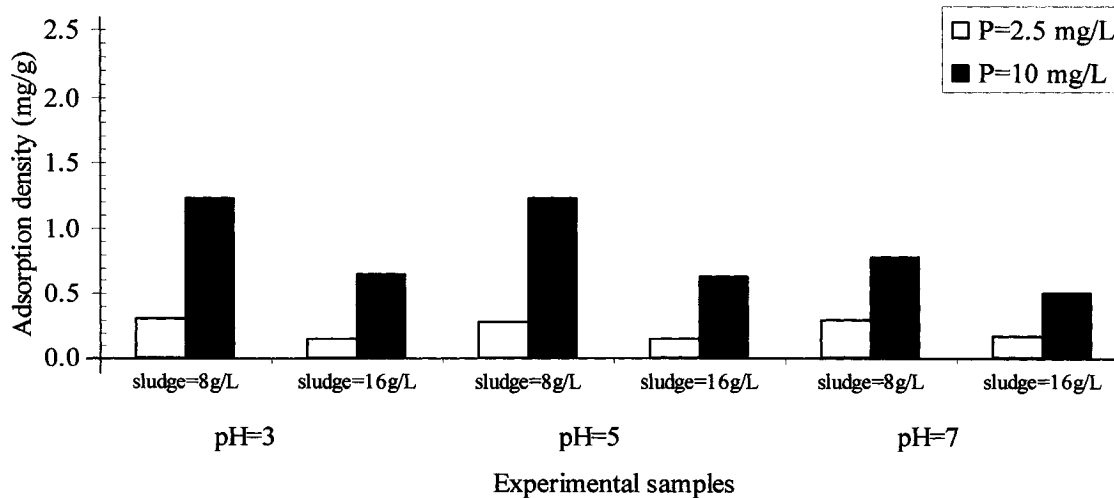
c) particle size =1180 μm

Figure 6-2. The effect of pH and initial phosphorus concentration on adsorption density

mostly below 0.5 mg/L for influent phosphorus of 2.5 mg/L (Figure 6-3). With a few

exceptions most of effluent phosphorus concentrations were less than 1 mg/L for influent

phosphorus concentration of 10 mg/L. Duplicate experimental results showed similar

findings (Appendix A).

The relative significance of oven dried alum sludge concentration and pH conducted

using ANOVA test indicated that the effect of pH on the changes in effluent phosphorus

concentration was mostly insignificant (Table 6-1). Appendix D provides a detailed

analysis of the ANOVA. High oven dried alum sludge concentrations were found to be

significant for decreased effluent phosphorus concentrations.

Table 6-1. ANOVA for five alum sludge concentrations and three pH levels (Initial

phosphorus = 2.5 mg/L and particle size = 250 μm)

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.1226	6.53066	5678.83	0.000
pH	0.0009	0.00043	0.37	0.694
Interaction	0.0123	0.00154	1.34	0.297
Residual	0.0172	0.00115	—	—

The effluent pH was understandably dependent on the influent pH. An influent pH 3

produced effluent pH of 3-4 (Figure 6-4). Similarly an influent pH 5 generated an

effluent pH range 4.5-5.5 and an influent pH 7 generated an effluent pH range of 6-7.5.
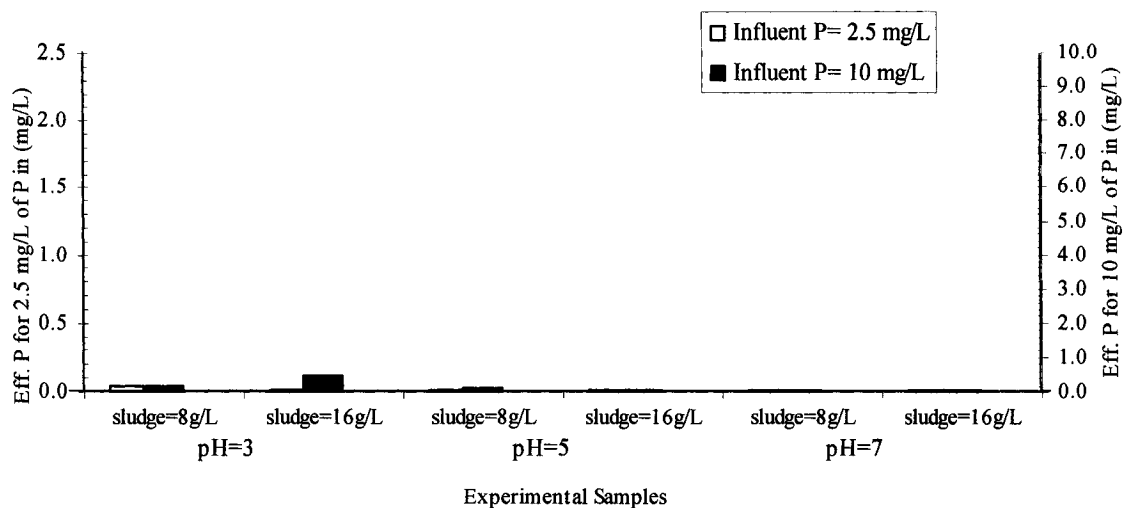
a) particle size =250 μm
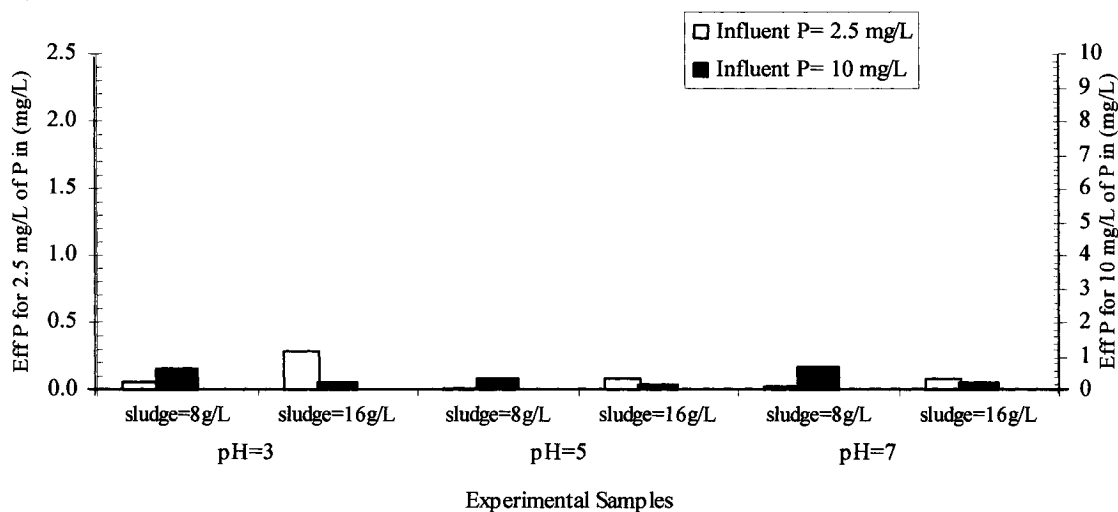
b) particle size =425 μm
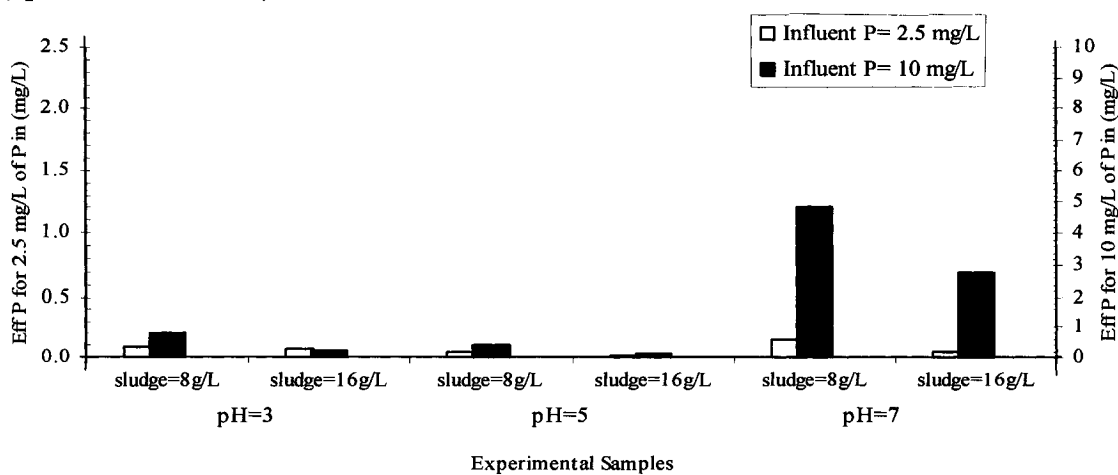
c) particle size =1180 μm
Figure 6-3. The effect of pH and initial phosphorus concentration on effluent phosphorus

An effluent pH of 3-4 is not suitable for disposal in surface water. The effluent pH can be increased prior to disposal in surface water. However, the cost of chemicals to reduce the initial pH and to increase the final pH and the hazards of dealing with increased amount of sludge would pose negative interest for pH control.

6.3.3 Effect of initial phosphorus concentration

As evidenced from the experimental results, oven dried alum sludge was effective in removing phosphorus at various concentrations tested. However, a high initial phosphorus concentration (10 mg/L) appeared to generate consistently higher adsorption density than low initial phosphorus concentration (2.5 mg/L) (Figure 6-2) (Detail experimental results are in Appendix A). It was understandable as, there was more phosphorus in the same volume of wastewater available in the high initial phosphorus concentration than that of low initial phosphorus concentration. The adsorption density generated in an alum sludge concentration of 8 g/L appeared to have consistently more adsorption density than 16 g/L of alum sludge. It was probably because 16 g/L of alum sludge provided more alum sludge than needed for an efficient adsorption.

Effluent phosphorus concentrations were high for high initial phosphorus concentrations (Figure 6-3), which was due to large amount of phosphorus being available for tests conducted in high initial phosphorus concentration. Appendix A provides detailed P concentrations for these experiments. Among a few exceptions, at a pH of 7, low initial phosphorus concentrations had much higher phosphorus removal than that of high initial
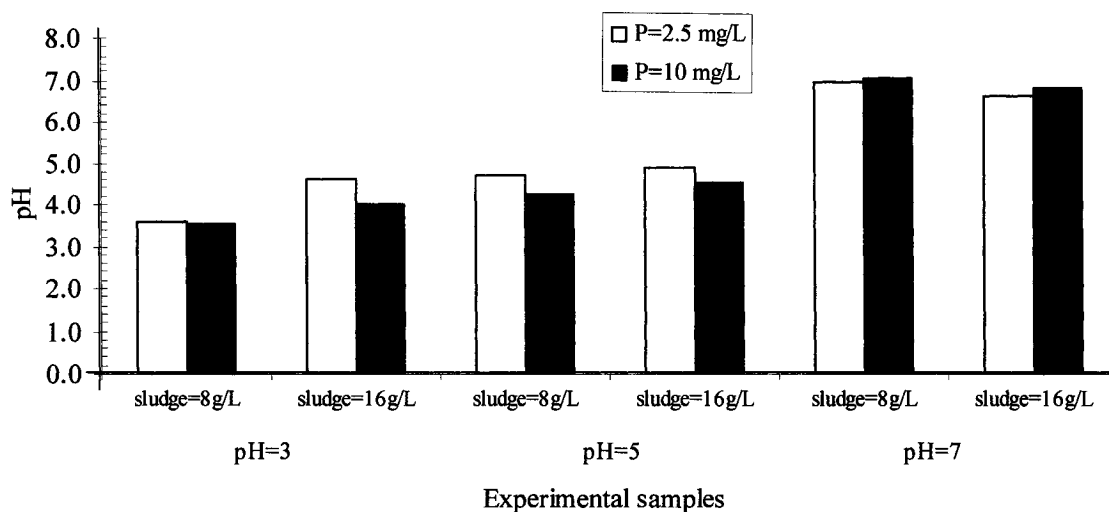
a) particle size =250 μm
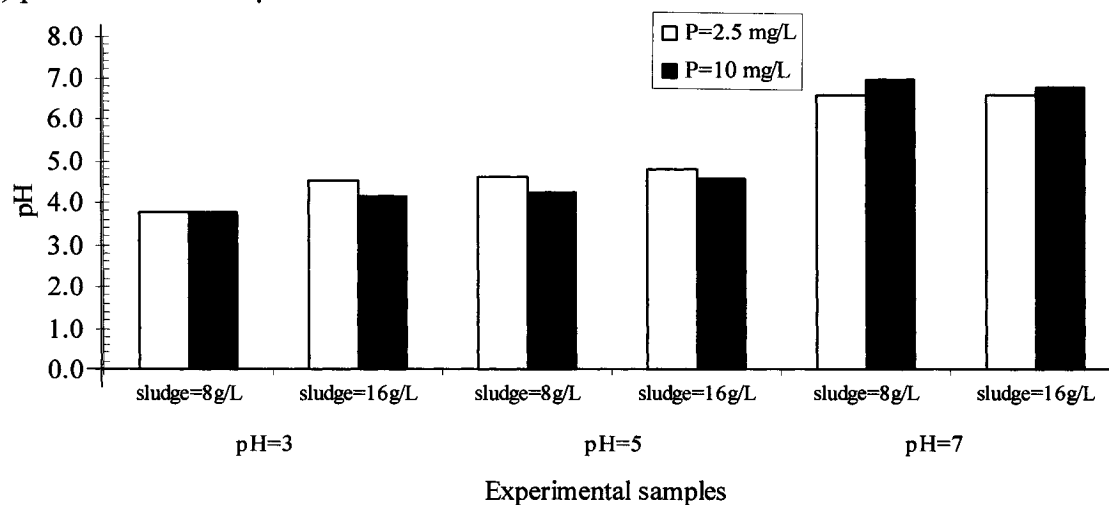
b) particle size =425 μm
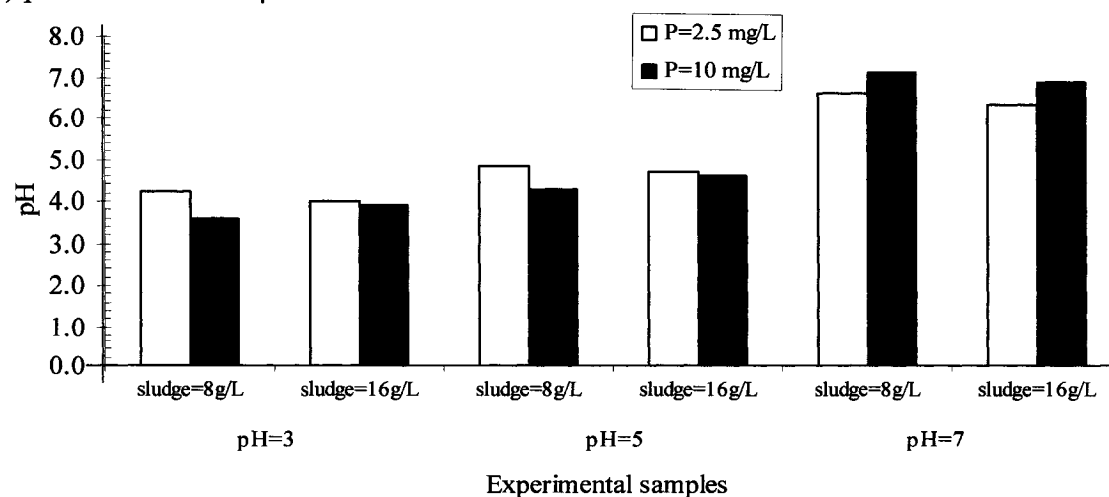
c) particle size =1180 μm

Figure 6-4. The effect of pH and initial phosphorus concentration on effluent pH

phosphorus concentrations. This indicated the possibility of chemical adsorption mechanism involved orthophosphate adsorption on oven dried alum sludge. The results implied that alum sludge can be used to adsorb phosphorus at variable concentrations.

6.3.4 Effect of particle size

The experimental results showed higher adsorption density for fine particles than coarse particle sizes for all the three pH tested (Figure 6-5). This was probably because fine particles had more surface area than coarse particle sizes and adsorption being a surface phenomenon was affected by the particle sizes. Particle size did not have any considerable effect at a pH of 5. At a solution pH of 7, fine particles (250 μm) had considerably higher adsorption densities than other pHs, in particular at high phosphorus concentrations (10 mg/L). It was probably due to variability in surface activity at various pHs tested.

Effluent phosphorus concentrations with a few exceptions were higher for a particle size of 1180 μm than other finer particles (Figure 6-6). ANOVA test conducted on the effect of particle size on the effluent phosphorus concentrations showed mixed results for various pHs (Appendix D). For an influent pH 7, particle size was significant in explaining the variability in effluent phosphorus concentrations (Table 6-2). For influent pH 5, the effect of particle size was statistically insignificant. Understandably phosphorus removal was affected with the variation in particle sizes. Phosphorus removals in fine particles (250 μm) were better than coarse particles. The effluent pH values were not affected considerably with the changes in particle sizes (Figure 6-7).
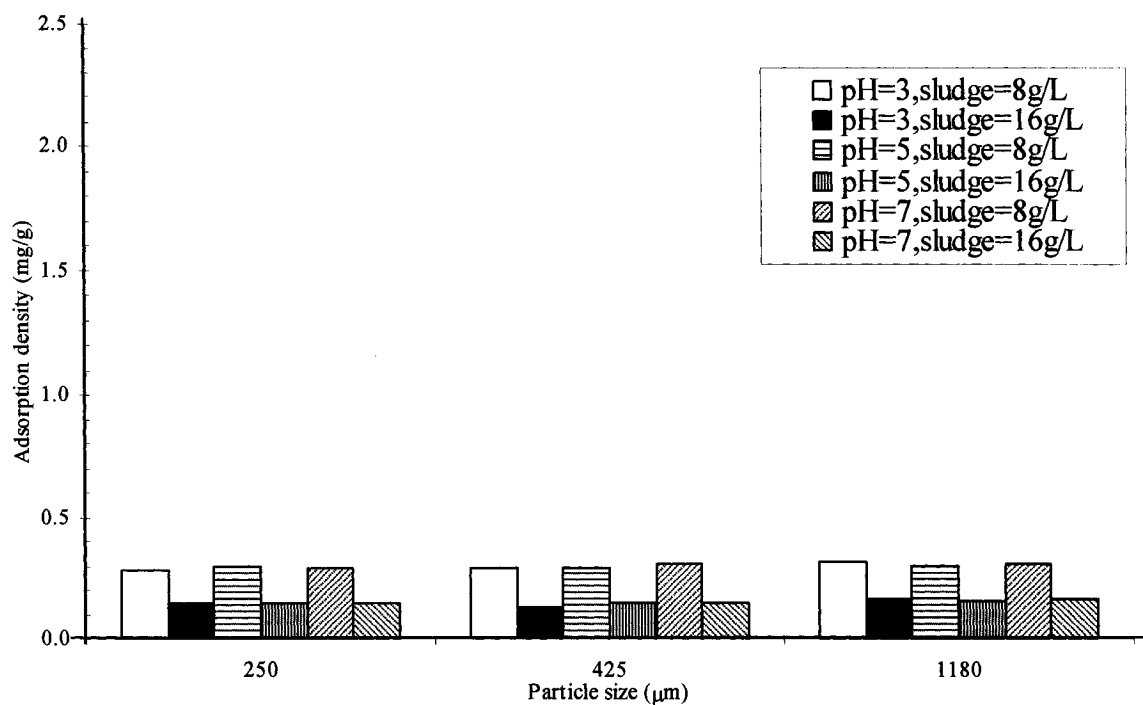
a) Initial phosphorus = 2.5 mg/L
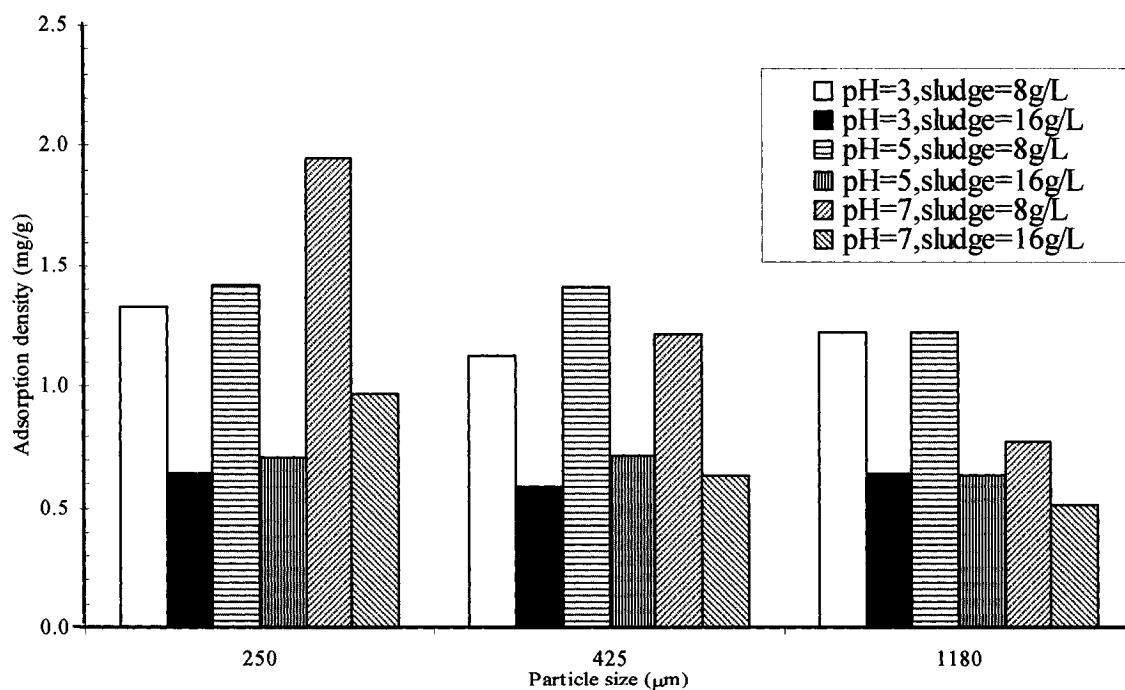
b) Initial phosphorus = 10 mg/L

Figure 6-5. The effect of particle size on adsorption density
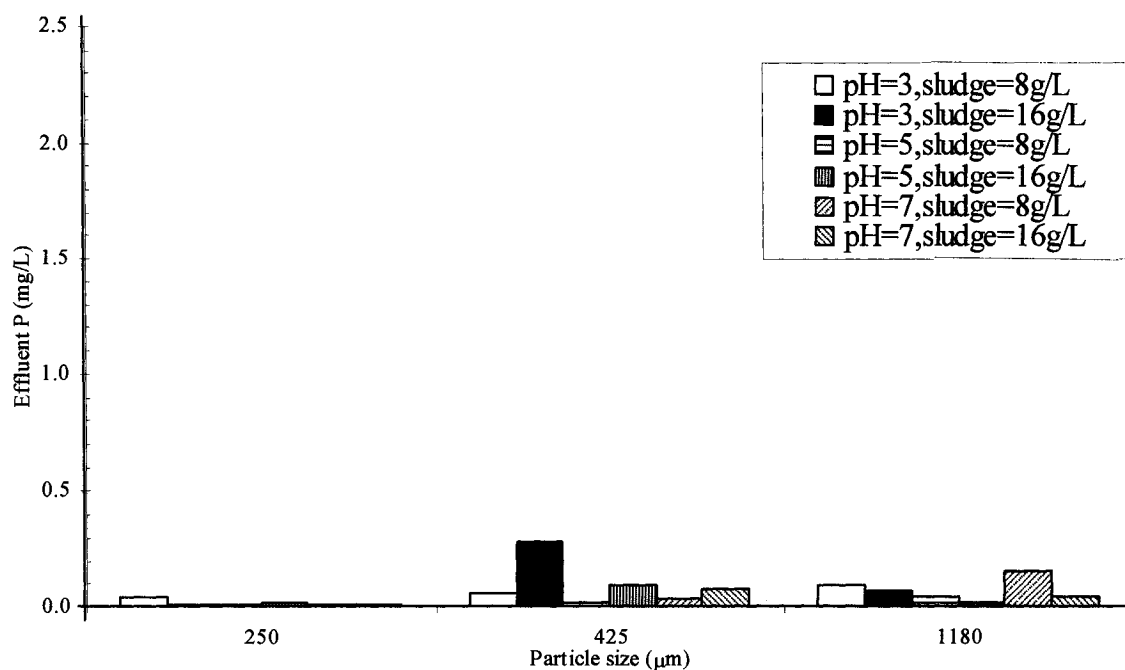
a) Initial phosphorus = 2.5 mg/L
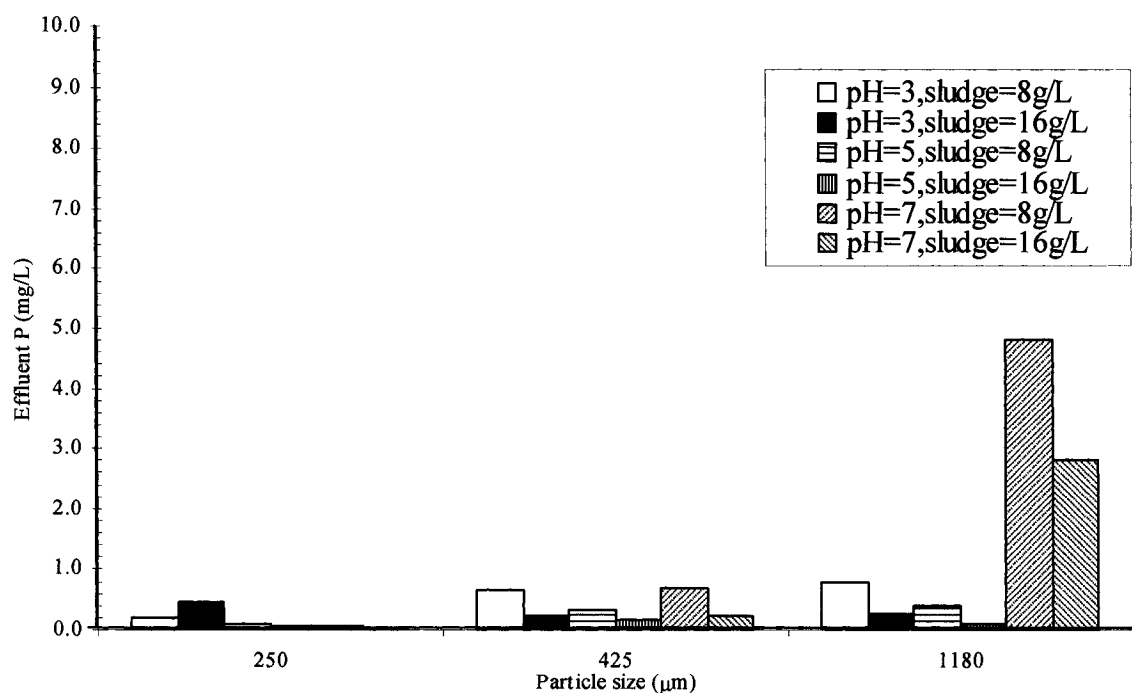
b) Initial phosphorus = 10 mg/L

Figure 6-6. The effect of particle size on effluent phosphorus concentration
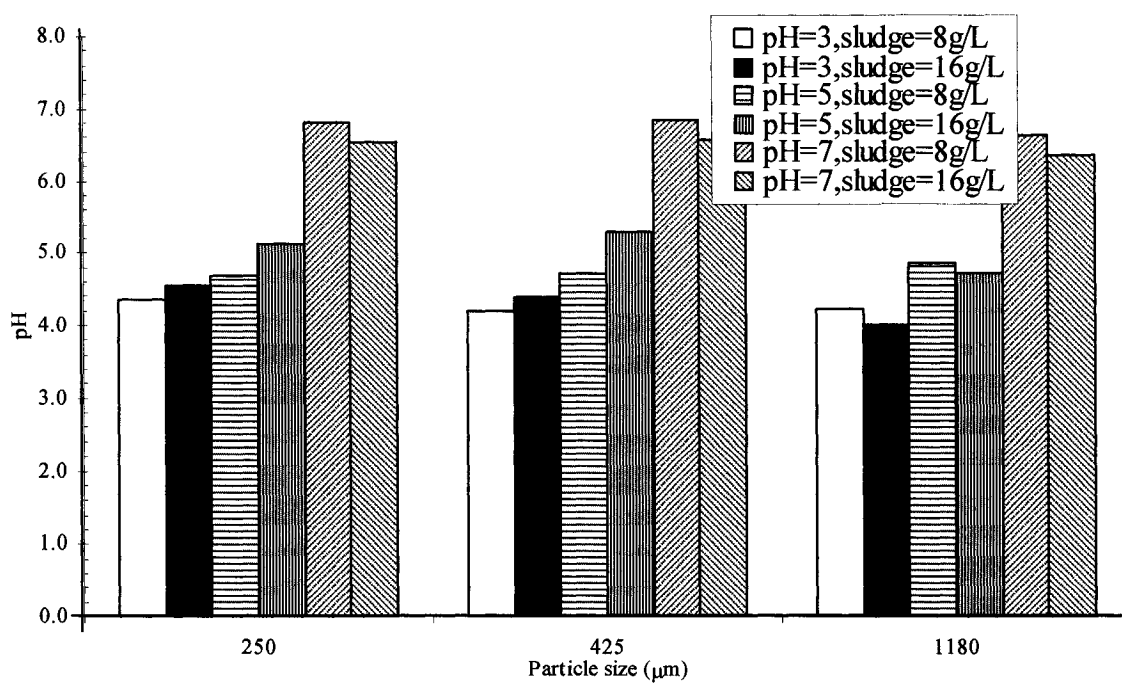
a) Initial phosphorus = 2.5 mg/L
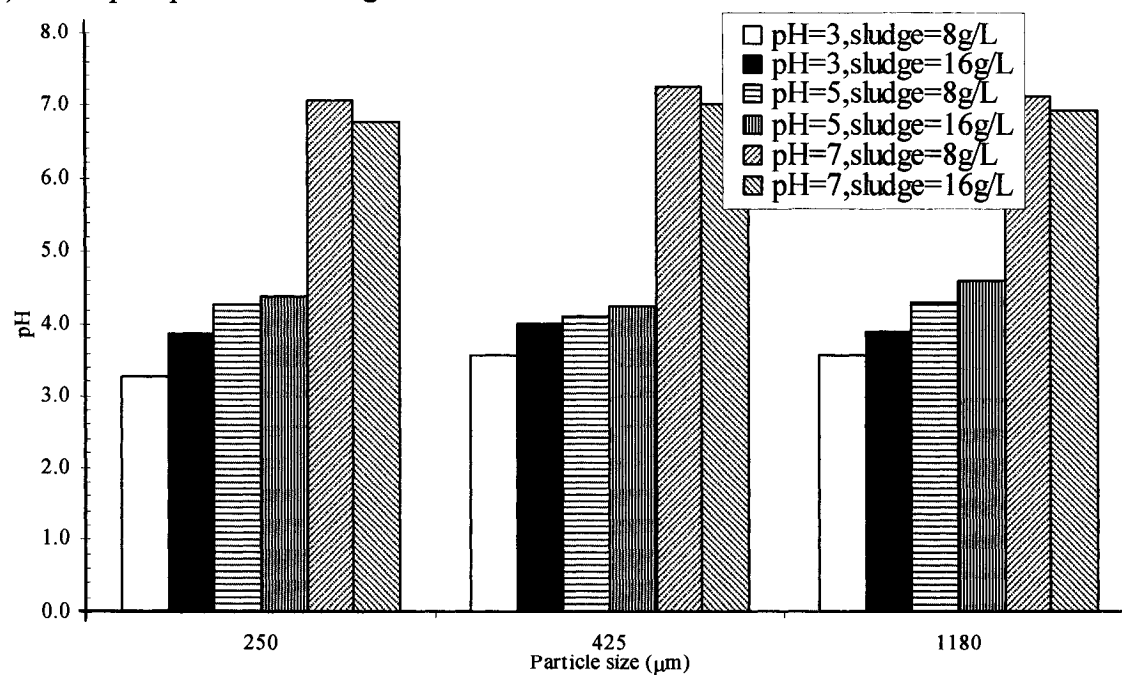
b) Initial phosphorus = 10 mg/L

Figure 6-7. The effect of particle size on effluent pH

Table 6-2. ANOVA for five alum sludge concentrations and three particle sizes (Initial phosphorus = 2.5 mg/L and pH = 7)

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.8033	6.70082	522.82	0.000
Particle size (mm)	0.1810	0.09050	7.06	0.007
Interaction	0.1933	0.02416	1.89	0.138
Residual	0.1922	0.01282	—	—

6.3.5 Treatment of small-scale wastewater

6.3.5.1 Treatment of Secondary Municipal Effluent

Experimental results showed that oven dried alum sludge was effective in removing phosphorus from secondary municipal effluent (Figure 6-8). The Langmuir adsorption isotherm equation was not effective in predicting adsorption density of total phosphorus (Table 6-3). Freundlich isotherm equations were effective in predicting partitioning in solid and liquid (Figure 6-9). The values of Freundlich isotherm parameter, K_d was comparable and even better than the values observed with deionized water in Chapter 5. In general, K_d values were higher in orthophosphates than in total phosphorus. The value of n for orthophosphates was lower in municipal wastewater than in deionized water, indicating slow increase in adsorption density with the increase in solution concentration. The Langmuir isotherm equation also computed a maximum adsorption density, Q_{max} of 3.212 mg P/g for orthophosphates, which was much higher than that found in Chapter 5.
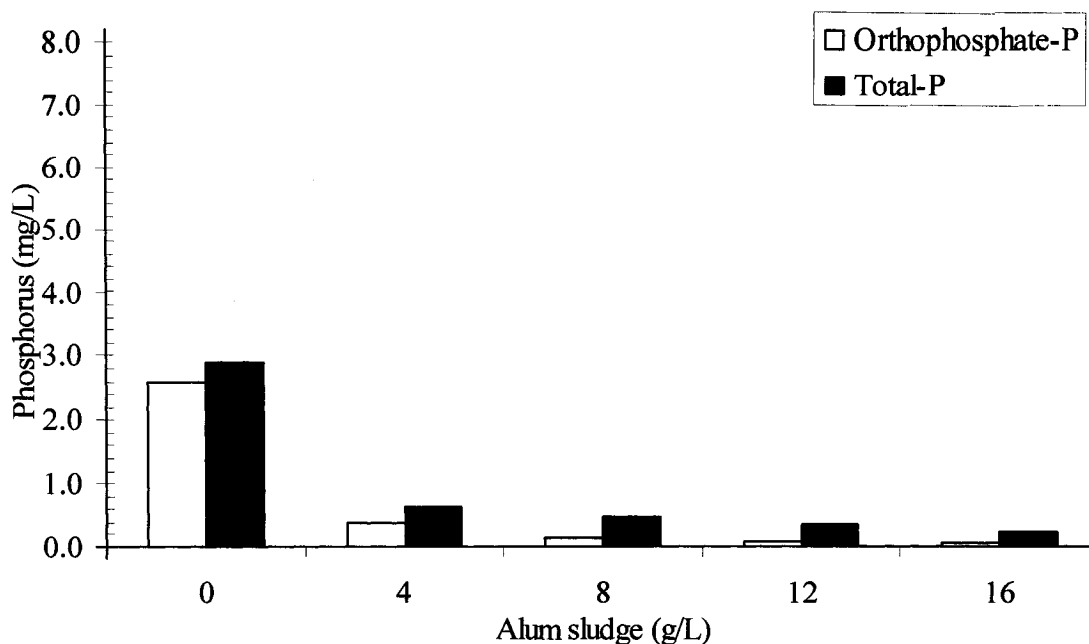
Figure 6-8. Effluent phosphorus concentration in batch tests on municipal effluent

The effluent pH values observed after batch experiments were in the range of 5.69-6.16

(Table 6-4). The results indicated a decrease in the pH values from 7.23 with an increase

in alum sludge concentration. In general, a pH value in the range of 6-9 is reasonable for

wastewaters before disposal into surface water. However, fixed bed column tests results

discussed in the next chapter would be more suitable in explaining the surface water

disposal criteria as those tests were dynamically similar to wastewater treatment facilities.

Table 6-3. Coefficients of Freundlich and Langmuir adsorption isotherms

Tests	Freundlich			Langmuir		
	R^2	K_d	N	R^2	Q_{max} (mg P g^{-1})	K (L g^{-1} P)
Secondary Municipal Effluent						
Orthophosphate	0.98	0.961	0.61	0.93	3.212	0.294
Total phosphorus	0.93	0.826	1.22	0.39	0.538	-2.211
Pilot scale biofiltration effluent						
Orthophosphate	0.87	0.832	0.246	0.96	3.51	0.369
Total phosphorus	0.72	0.813	0.226	0.82	2.44	0.581
Bench scale biofiltration effluent						
Orthophosphate	0.98	4.138	1.0864	0.39	3.12	-1.47
Total phosphorus	0.94	3.917	1.9339	0.89	0.85	-0.874
Aquaculture process water						
Orthophosphate	0.96	1.358	0.6321	0.72	7.1123	0.0794
Total phosphorus	0.71	0.265	0.7101	0.17	0.4242	1.5647
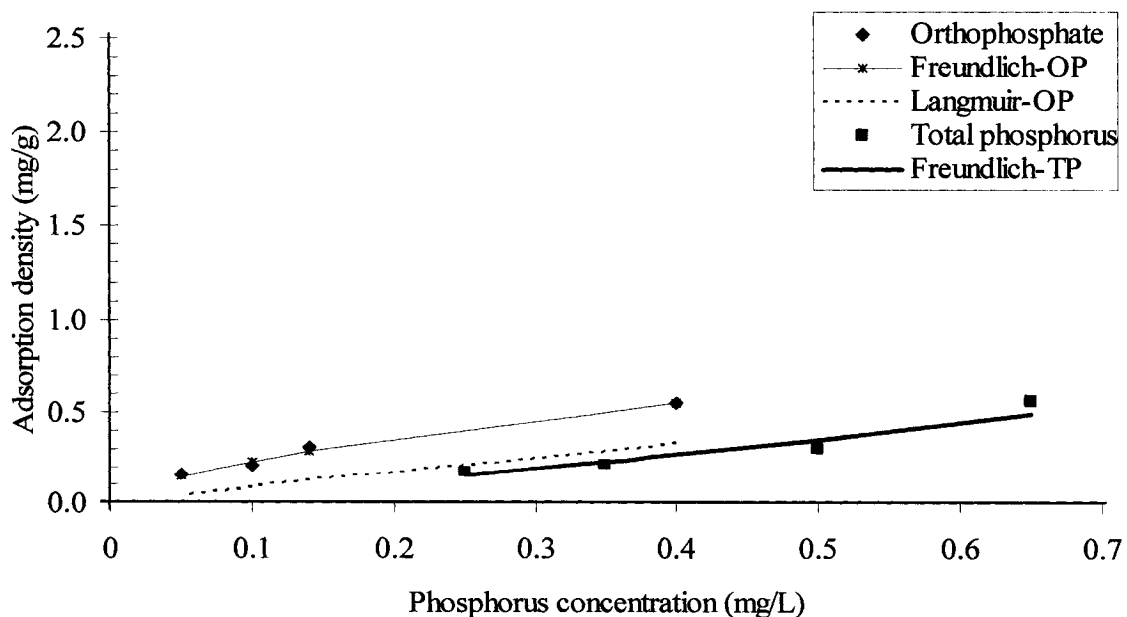
Figure 6-9. Adsorption isotherm in secondary municipal wastewater effluent

Table 6-4. Effluent pH after batch experimental results

Adsorbent (g/L)	0	4	8	12	16
Secondary municipal effluent	7.23	6.16	5.85	5.71	5.69
Pilot scale biofiltration effluent	6.48	5.36	5.79	5.93	5.94
Bench scale biofiltration effluent	6.62	5.31	5.71	6.19	6.23
Aquaculture process water	7.75	6.55	6.23	5.91	6

6.3.5.2 Treatment of On-site Decentralized Wastewater

The experimental results showed that oven dried alum sludge was also effective in removing phosphorus from decentralized on-site wastewater (Figure 6-10). The Langmuir adsorption isotherm equations were not effective in predicting bench scale biofiltration wastewater (Table 6-3). Freundlich isotherm equations were effective in predicting partitioning in solid and liquid phase for both types of biofiltration wastewater (Figure 6-11). Bench scale biofiltration wastewater showed a steep isotherm curve, indicating large values of Freundlich distribution coefficient, K_d, even greater than the values obtained with deionized water in Chapter 5. This also indicated high degree of phosphorus adsorption from bench scale biofiltration wastewater. The values of n were also higher in bench scale biofiltration wastewater than in pilot scale wastewater. However, the values of n were lower than the n values in deionized water. In general, K_d values were higher in orthophosphates than in total phosphorus. It indicated the possibility of higher adsorption of orthophosphate than total phosphorus. The Langmuir isotherm equation also computed a maximum adsorption density, Q_{max} higher in

orthophosphates than in total phosphorus for pilot scale biofiltration wastewater. The

value of Q_{max} was higher in biofiltration wastewater than that of deionized water.

Effluent pH measured at the end of the experiment showed a decrease with the addition

of oven dried alum sludge in the wastewater (Table 6-4). However, the decrease in pH

values could not be correlated with the weight of oven dried alum sludge addition. These

pH values were not suitable for disposal in surface water.
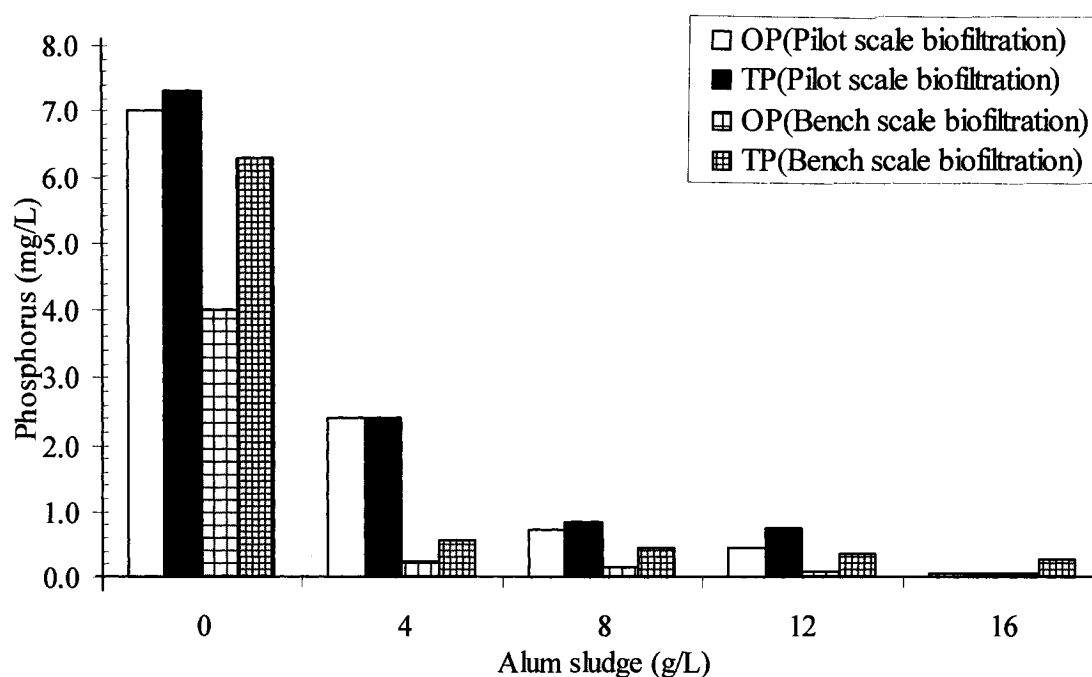
Figure 6-10. Effluent phosphorus concentration for batch tests on biofiltration wastewater

a) Pilot scale biofiltration effluent (orthophosphate)

b) Pilot scale biofiltration effluent (total phosphorus)

c) Bench scale biofiltration effluent (orthophosphate)

d) Bench scale biofiltration effluent (total phosphorus)
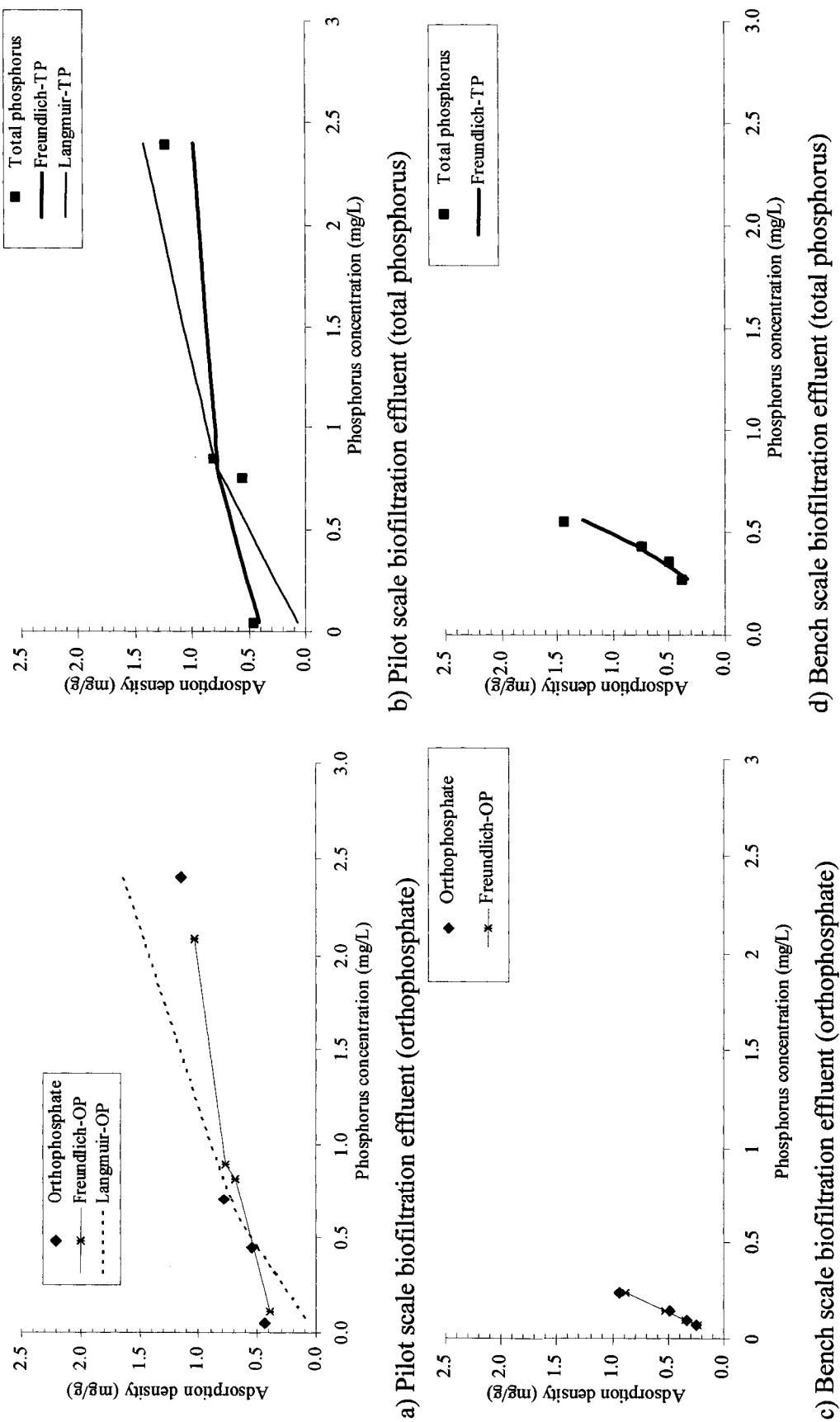
Figure 6-11. Batch adsorption isotherms in wastewaters from recirculating biofilter

6.3.5.3 Treatment of Aquaculture Process Water

The experimental results showed that oven dried alum sludge was effective in removing

phosphorus from aquaculture process water (Figure 6-12). However, the decrease in total

phosphorus concentration was smaller than that for orthophosphates. The Langmuir

adsorption isotherm equation was not effective in predicting both orthophosphate and

total phosphorus (Table 6-3, Figure 6-13). Freundlich isotherm equations were effective

in predicting adsorption density (Figure 6-13). The isotherm curve showed a large value
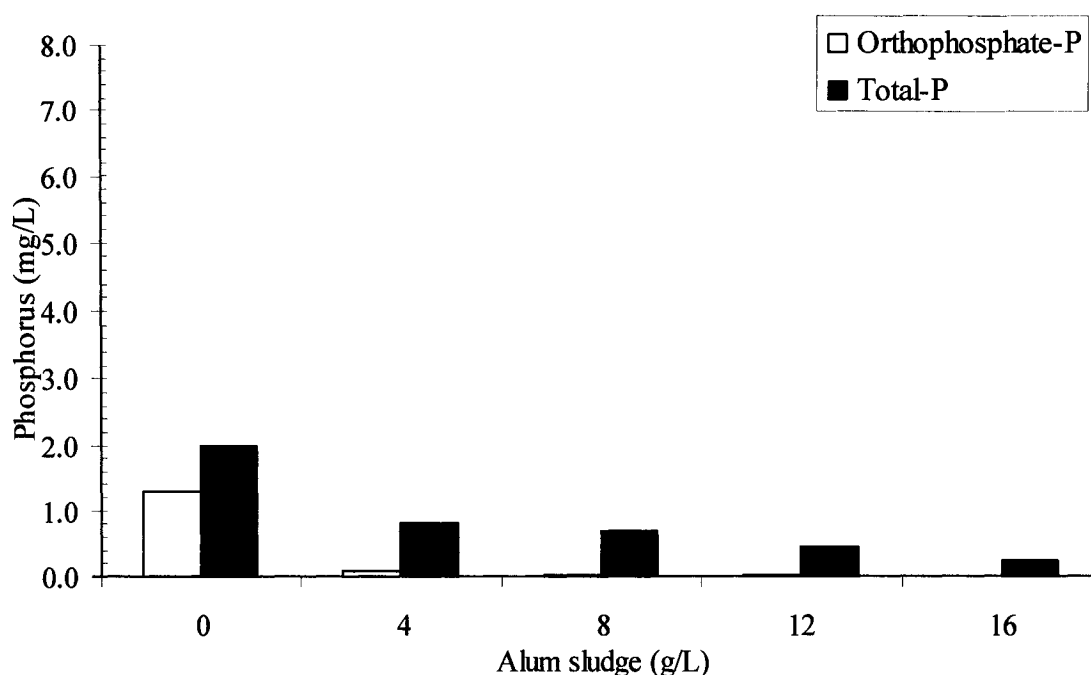
Figure 6-12. Effluent phosphorus concentration for batch tests on aquaculture wastewater

of Freundlich distribution coefficient, K_d, even greater than the values obtained with

deionized water in Chapter 5 for orthophosphate. The values of n were lower than that

found in Chapter 5 in deionized water. K_d value was higher in orthophosphates than that

of total phosphorus. Langmuir isotherm equations also computed a maximum adsorption

density, Q_{max} higher in orthophosphates than that of Q_{max} in biofiltration wastewater. pH

values measured at the end of the experiment showed a decrease with the addition of

alum sludge in the wastewater (Table 6-4). However, pH values were mostly greater than

6, indicating suitability in surface water disposal.
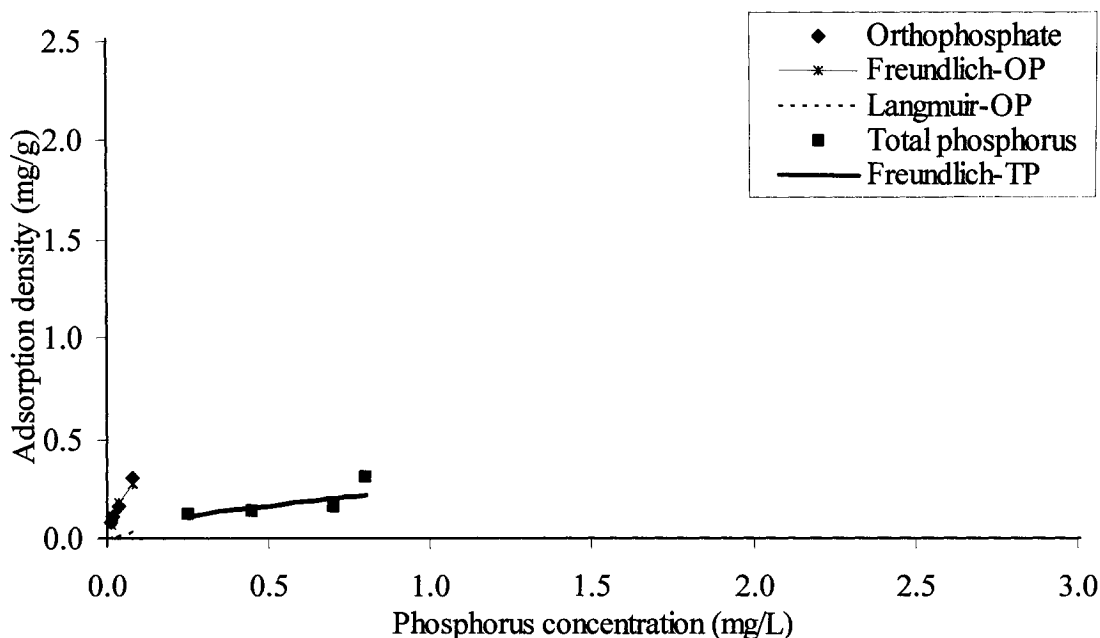
Figure 6-13. Batch adsorption isotherm on aquaculture process water

6.4 Conclusions

The batch adsorption tests were shown to be reproducible. A pH of 5 seemed to be the

most appropriate pH for phosphate adsorption on oven dried alum sludge. However, the

effect of pH in these studies was based on deionized water and the result was also mostly

statistically insignificant. Oven dried alum sludge was shown to be effective in removing

phosphorus from wastewaters having 2.5 mg/L and 10 mg/L of phosphorus. Fine

particles appeared to have the largest adsorption density and the highest phosphorus

removal. However, coarse particles were also showed to have considerable phosphorus

removal and adsorption density. The effect of particle size on effluent phosphorus concentration was statistically significant.

Oven dried alum sludge also appeared to have removed phosphorus from small-scale wastewater. The phosphorus removal capability of oven dried alum sludge from small-scale wastewater was comparable to phosphorus removal from deionized water. Adsorption density in small-scale wastewater was higher than adsorption density in deionized water for most tests conducted. It implied that the presence of competing ions in the wastewater was not considerable to affect the phosphorus adsorption in oven dried alum sludge. The removal of total phosphorus was not as effective as the removal of orthophosphates. Langmuir isotherms were not very effective in predicting adsorption densities on oven dried alum sludge. The values of the Freundlich parameters in small-scale wastewaters appeared to have high values compared to the Freundlich parameters found in deionized water in Chapter 5.

7.0 ADSORPTION KINETICS OF OVEN DRIED ALUM SLUDGE: RAPID SMALL-SCALE COLUMN TESTS

7.1 Introduction

Adsorption kinetics studies in batch systems were limited with static tests on adsorption capacities of oven dried alum sludge. However, adsorption treatment for wastewater is normally dynamic, as the production of wastewater is dynamic in nature. Fixed bed columns are the most widely used method for adsorption treatment of wastewater. In fixed bed columns, adsorbents remain static and wastewater is passed through the adsorbent. Intuitively, in the process of wastewater passing through oven dried alum sludge, phosphorus would be adsorbed onto the adsorbent and the effluent would be left without any phosphorus. The time it takes for phosphorus to leach is known as the breakthrough point. The effluent slowly reaches the phosphorus equal to the phosphorus level in the wastewater. In practice wastewater has phosphorus in limited quantities when it is disposed. In general, the regulatory bodies are responsible for setting the maximum phosphorus level allowed for specific wastewater disposal. The time it takes for the effluent to reach the maximum phosphorus level is known as the breakthrough time in practical applications, and will be used as the breakthrough pore volume in this project.

The objective of this chapter was to examine the phosphorus adsorption kinetics of oven dried alum sludge in a fixed bed column. Rapid small scale column tests (RSSCT) were used. The effects of pH, initial phosphorus concentration and particle size were investigated. Small-scale wastewaters as mentioned in Chapter 4 were also studied. The probable effluent pH levels were also investigated.

7.2 Experimental Procedure

Rapid small scale column tests (RSSCT) were used for fixed bed column tests, as they are known to provide results without causing errors due to scaling (Crittenden et al., 1986; Crittenden et al., 1987). Particle sizes were similar to that mentioned in Chapter 4. Breakthrough was identified as 0.1 mg/L of phosphorus for orthophosphate concentration and 0.2 mg/L for total phosphorus. Results expressed the variation in fraction leaching (effluent phosphorus concentration / influent phosphorus concentration) with the variation in pore volume process (volume of water processed / volume of pore space in a column). Aluminum and BOD_5 was measured as part of leaching behaviour of metal and organic matter.

Phosphorus removal was examined in oven dried alum sludge, granular activated carbon and blast furnace slag for comparative purposes with an initial phosphorus concentration of 2.5 mg/L as orthophosphate with identical environmental conditions. These experiments were repeated. The effects of particle size were examined on three different particle sizes on deionized water spiked with 2.5 mg/L phosphorus as orthophosphates. The particle sizes used were 0.73 mm, 0.98 mm and 1.20 mm. These tests were repeated. The effect of pH and initial phosphorus concentrations were measured using six column tests for two different initial phosphorus concentrations of 2.5 mg/L and 10 mg/L and three different pH levels of 3, 5 and 7. These tests were repeated. Small-scale wastewaters were also used for application of oven dried alum sludge to wastewater treatment. Four different types of wastewaters were used for column test. Secondary

municipal effluent and aquaculture process water were tested with three different pH levels of 3, 5 and 7. pH was controlled using HCl and NaOH. Two tests were conducted using pilot scale biofiltration wastewater with a pH level of 5 and 6.5. Two tests were conducted using bench scale biofiltration wastewater without any pH treatment. Reproducibility of the experimental result was tested by using six sets of data for samples at identical environmental conditions. Influent phosphorus concentrations were 2.5 mg/L of phosphorus with a pH of 5.5.

Statistical analysis was conducted using one-way ANOVA on phosphorus concentration obtained at variable pH and also on phosphorus concentration obtained at variable particle sizes. As there were only two different initial phosphorus concentrations were used, ANOVA was not conducted on variability of initial phosphorus concentrations. Experimental results from repetitive experiments were also used in ANOVA.

7.3 Results on Applicability of Oven Dried Alum Sludge as a Phosphorus Adsorbent

7.3.1 Reproducibility

As showed in Figure 7-1, the reproducibility was consistent throughout a given column experiment. Standard deviations ranged from 0.00009 to 0.1384 for an average fraction leaching of 0.0012 to 0.5282. At 95 pore volume processed, the samples were collected and tested later; inconsistent sampling procedures might have caused high standard deviation. It was able to identify the breakthrough point (0.1 mg/L of phosphorus) without any error.
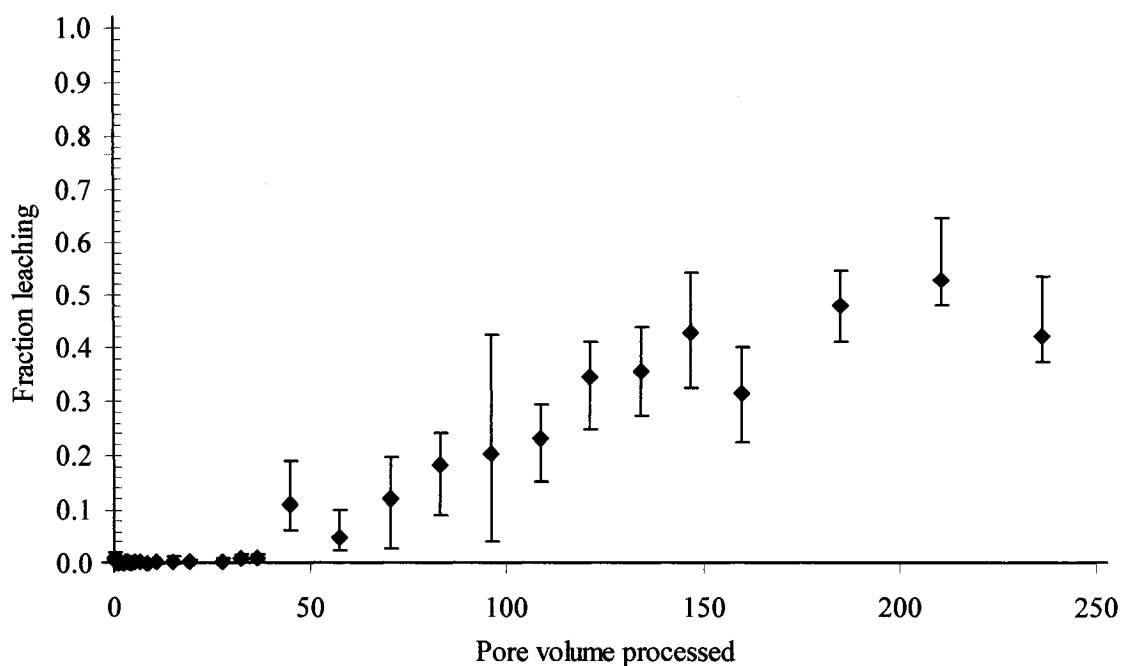
Figure 7-1. Reproducibility of fixed bed column experiments at 2.5 mg/L of P in 5%

level of significance

7.3.2 Oven dried alum sludge compared to other conventional adsorbents

Oven dried alum sludge was able to remove phosphorus comparable to other

conventional adsorbents (granular activated carbon) tested (Figure 7-2). Previous studies

conducted on air dried alum sludge also observed effective phosphorus removal (Huang

and Chiswell, 2000; Kim et al., 2003a). Blast furnace slag was able to remove

phosphorus consistently throughout the experimental periods. However, the effluent pH

for blast furnace slag was higher than 10 for most of the times for an influent pH of 5.5

(Figure 7-2). This was because the deionized water did not have any buffering capacity

and the increase in pH was probably the reason for the high removal in blast furnace slag.

Previous studies conducted on blast furnace slag also observed similar phosphorus

removal capability (Johansson and Gustafsson, 2000; Sakadevan and Bavor, 1998;

Yamada et al., 1986). Batch adsorption test results for blast furnace slag at a lower pH

level were less effective than alum sludge. However, high pH was also not suitable for

disposal of effluent in surface water. Repetitive experiments did show similar

experimental findings (Appendix B).
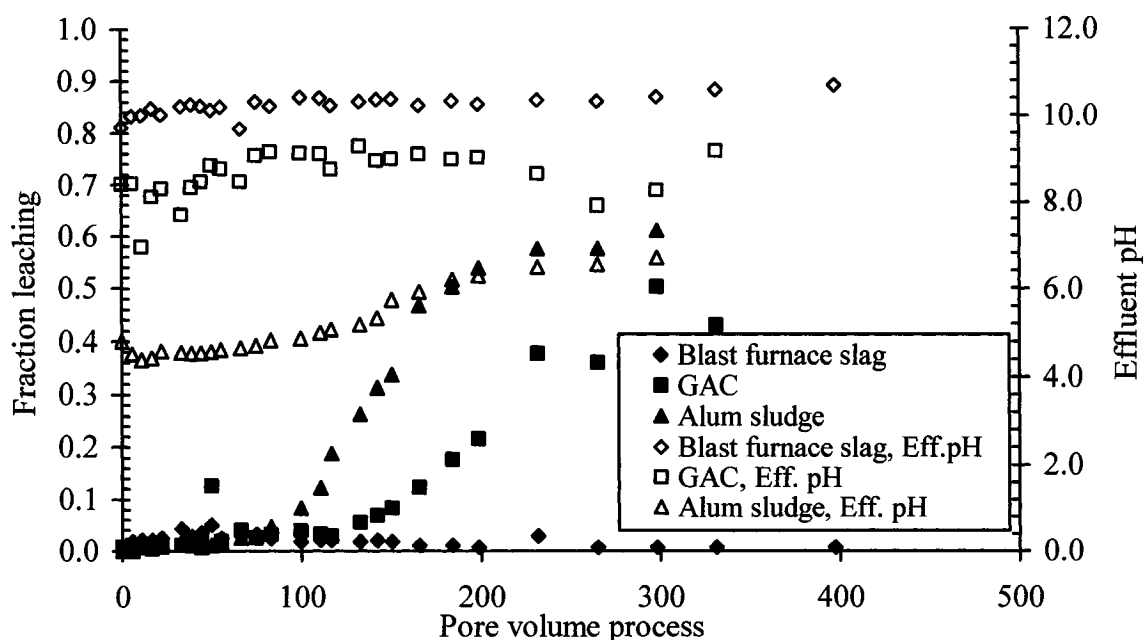
Figure 7-2. Phosphorus removal and effluent pH after adsorption in different materials

There were no definite patterns for the effluent BOD_5 (Figure 7-3). However, the effluent

BOD_5 for oven dried alum sludge was lower than GAC and blast furnace slag in many

cases. It indicated that oven dried alum sludge would be less likely to leach organic

matter than other conventional adsorbents.
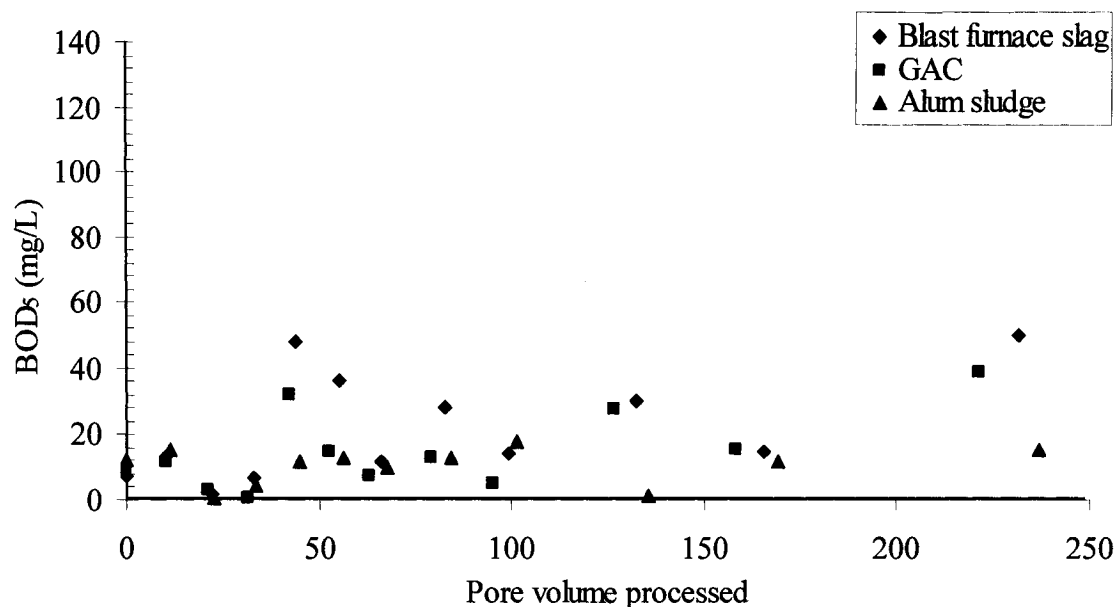
Figure 7-3. Biological oxygen demand in effluent after adsorption in different materials

7.3.3 Effect of particle size

The experimental results showed that fine particle sizes, in general, had a higher

phosphorus adsorption capacity than coarse particle sizes (Figure 7-4). This was

consistent with the finding from the batch test results and was due to large surface area of

fine particles. Breakthrough pore volumes as identified from the experimental results

were 106, 85 and 55 for particle sizes of 0.73 mm, 0.98 mm and 1.2 mm respectively.

Particle size did not have any considerable effect on the effluent pH (Figure 7-4).

However the effluent pH was low as the influent pH tested were 5 and deionized water

had little buffering capacity to resist the drop in pH level. Repetitive experimental results

also confirmed of these experimental findings. ANOVA test result indicated that the

effect of particle size on the breakthrough pore volume was significant (Table 7-1).
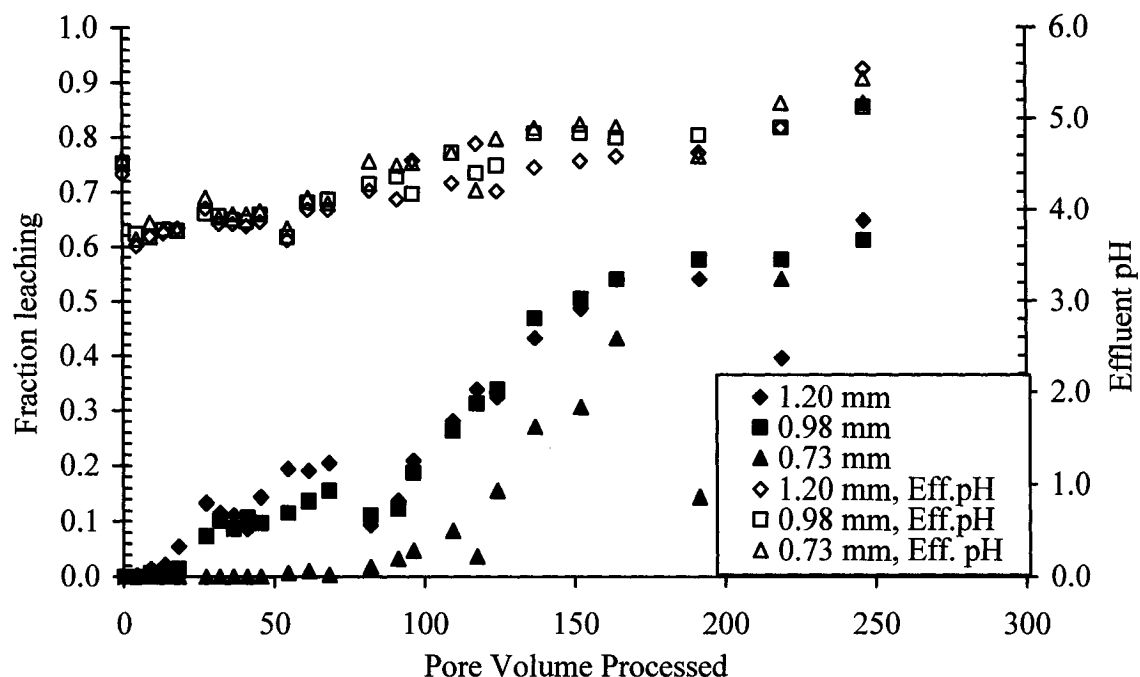
Figure 7-4. The effect of particle size on the phosphorus removal and effluent pH at an influent pH of 5

Table 7-1. ANOVA test for three particle sizes (Initial P = 2.5 mg/L and pH = 5.5)

Source	Sum of Square	Mean Square	F value	p value
Particle size (mm)	3193	1597	15.83	0.025
Residual	303	101	—	—

Aluminum leaching was higher in fine particles than coarse particles (Figure 7-5). It was understandable as the fine particles had larger surface area making it susceptible to leaching of aluminum with the interaction of deionized water. Aluminum leaching was high (>4mg/L) in the beginning of the experiment and decreased rapidly to less than 1 mg/L. The leaching of organic matter, as evidenced by BOD_5 was not affected by the

particle size. With an exception of BOD_5 value of 45, most of the samples tested had

BOD_5 values lower than 30 mg/L.
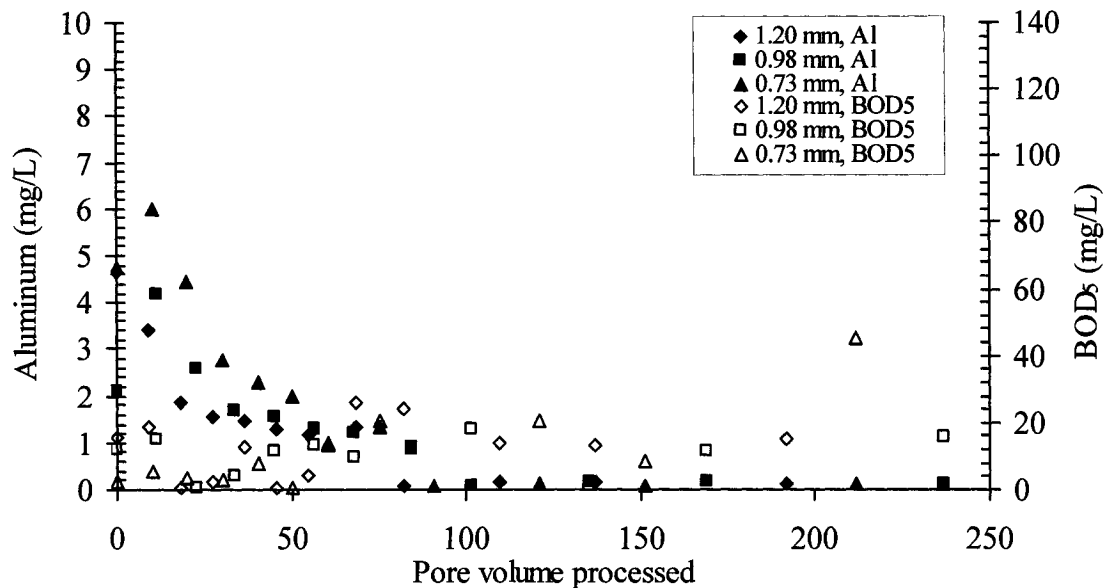
Figure 7-5. The effect of particle size on the leaching of aluminum and organic matter

7.3.4 Effect of pH

As evidenced from the experimental results, a pH of 3 had consistently removed

phosphorus for both types of initial phosphorus concentration tested (Figure 7-6). It was

consistent with a previous study conducted by Kim et al. (2003a). However, they

observed breakthrough pore volumes (700) much higher than that observed during this

study. It was probably due to differences in characteristics of alum sludge components

and particle sizes. There were no descriptions of treatment process options, source water

quality and particle sizes provided. Therefore, it was not possible to understand the

differences in alum sludge composition between these two sources. The experimental

results here also revealed that pH 5 had the largest breakthrough pore volumes for both

initial phosphorus concentrations (Table 7-2). However, once phosphorus leaching

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

Fraction leaching

0   100   200   300   400   500   600

Pore volume processed

◆ pH=3, P=2.5 mg/L
▲ pH=5, P=2.5 mg/L
■ pH=7, P=2.5 mg/L
◇ pH=3, P=10 mg/L
△ pH=5, P=10 mg/L
□ pH=7, P=10 mg/L
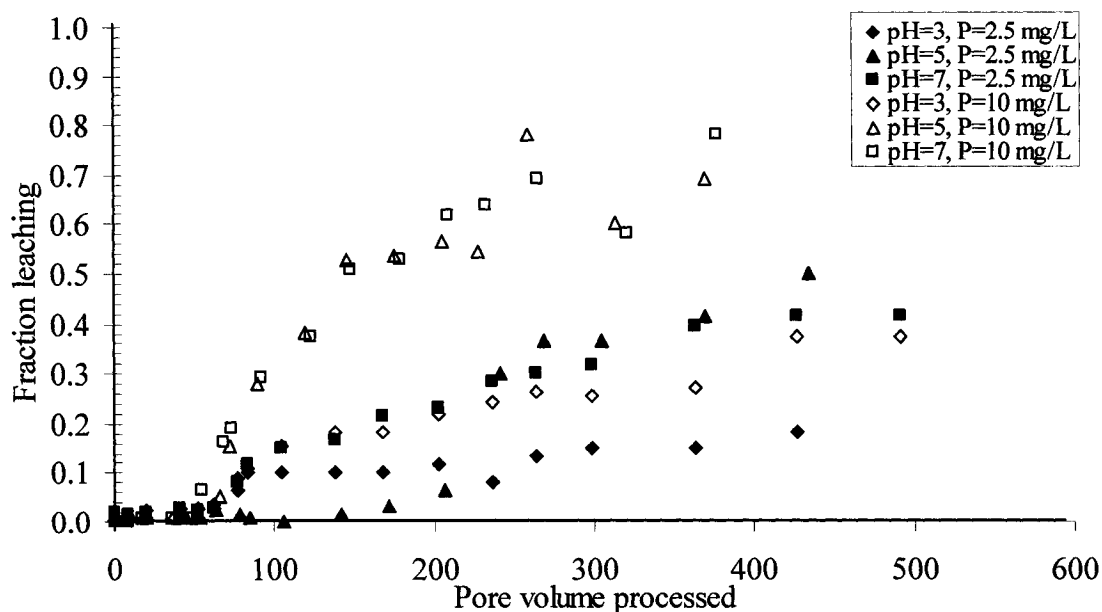
Figure 7-6. Effect of pH and initial phosphorus concentration on the phosphorus removal

Table 7-2. Effect of pH and initial phosphorus on breakthrough pore volume processed

Initial P / pH	3	5	7
2.5	77	171	77
10	62	67	55

broke through, the phosphorus concentration in the effluent increased rapidly to reach

exhaustion. A study conducted by Kim et al. (2003a) found similar breakthrough pore

volume processed (190) as this study at pH 5. The fraction leaching was higher in high

initial phosphorus concentration than in low initial phosphorus concentration. Repetitive

experimental results also supported these findings (Appendix B). ANOVA test indicated

that for low initial phosphorus concentration the effect of pH on the breakthrough pore

volume was significant (Table 7-3). However, the effect for the high initial phosphorus concentration was not significant.

Aluminum leaching was the largest at a pH of 3 for both initial phosphorus concentrations (Figure 7-7). It was because metal leaching was high in acidic environment. However, leaching of aluminum at other pHs were less than 2 mg/L, compared to more than 20 mg/L of aluminum leaching for pH 3. There was no considerable differences between the leaching at pH 5 and 7. However, Kim et al. (2003a) observed higher aluminum leaching than this study for similar test condition. They also did not observe any considerable change in leaching due to changes in pH. There were no definite pattern for organic leaching at different pH levels tested (Figure 7-8). It indicated no definite pattern for the leaching of organic matter. There were no definite effects shown by the differences in pH levels.

Table 7-3. ANOVA for three pHs (particle size=0.98mm)

Source	Sum of Square	Mean Square	F value	p value
Initial phosphorus = 2.5 mg/L				
pH	12153	6076.5	274.13	0.000
Residual	66.5	22.2	—	—
Initial phosphorus = 10 mg/L				
pH	240.3	120.2	7.67	0.066
Residual	47.0	15.7	—	—
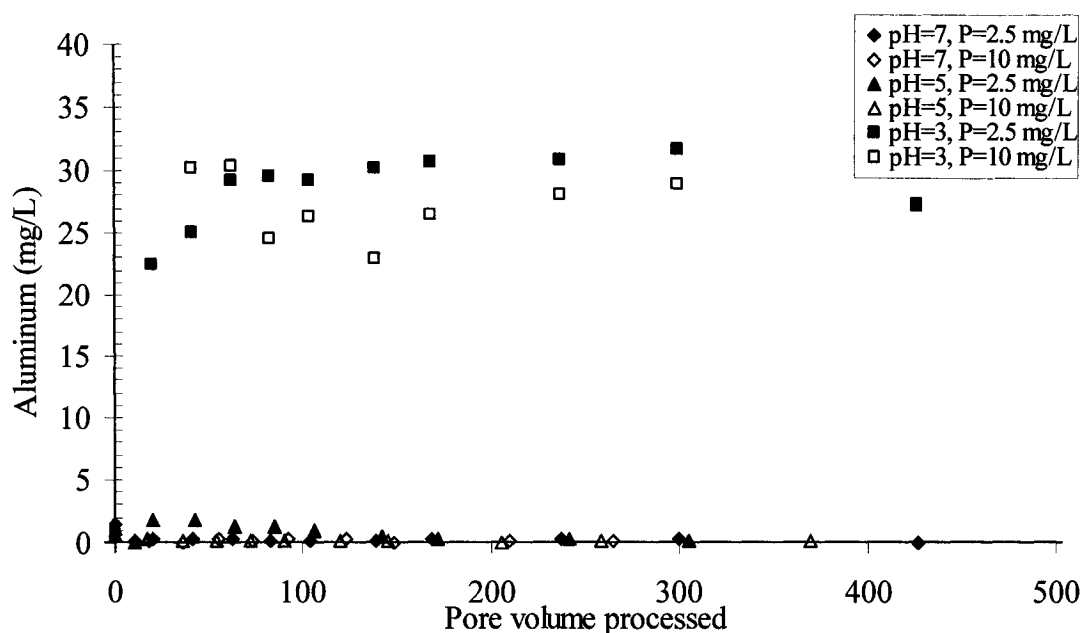
Figure 7-7. Effect of pH and initial phosphorus concentration on the aluminum leaching

Influent pH had considerable effect on the effluent pH levels (Figure 7-9). For an influent pH of 3, effluent pH was mostly in the range of 3-4. An influent pH of 7 had an effluent pH started around 5.5 and rose to 6.5 at the end of the experiment. The effluent pH values for an influent pH of 5 were 4.5 in the beginning of the experiment and rose to 6.5 at the end of the experiment. It was due to the adsorption and desorption of H^+ ions during the adsorption of phosphorus on alum sludge.
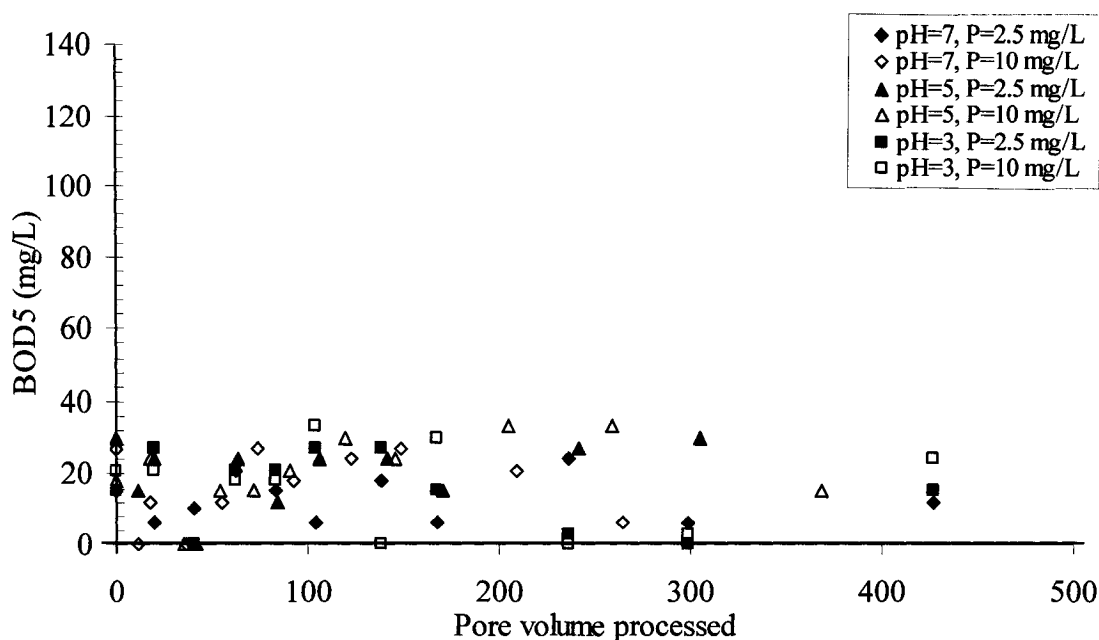
Figure 7-8. Effect of pH and initial phosphorus concentration on the organic matter

leaching

7.3.5 Effect of initial phosphorus concentration

As evidenced from the experimental results, high initial phosphorus concentrations had

earlier breakthrough and also consistently leached higher fraction than that of a low

initial phosphorus concentration (Figure 7-6). It was understandable as high phosphorus

concentration would be adsorbed onto the adsorption sites fast and would leach more

than that of low phosphorus concentrations. The results were consistent for all the pH

tested during the experiments. There were no considerable effects on aluminum leaching

by initial phosphorus concentration (Figure 7-7). It implied that the available phosphorus

for adsorption did not affect the available aluminum for leaching. Similar to aluminum,

the leaching of organic matter as evidenced from the experimental results was not

affected by variation in the initial phosphorus concentrations (Figure 7-8). There were no

link between phosphorus adsorption and organic matter leaching. This was because

organic matter present in alum sludge did not compete with phosphate for adsorption

sites. A previous study conducted on aluminum hydroxide also did not find competitive

adsorption between phosphate and soluble organic matter (Guan et al., 2005). There were

no effects observed in the effluent pH levels with the variation of initial phosphorus

concentrations (Figure 7-9). Repetitive experimental results were comparable to these

findings.
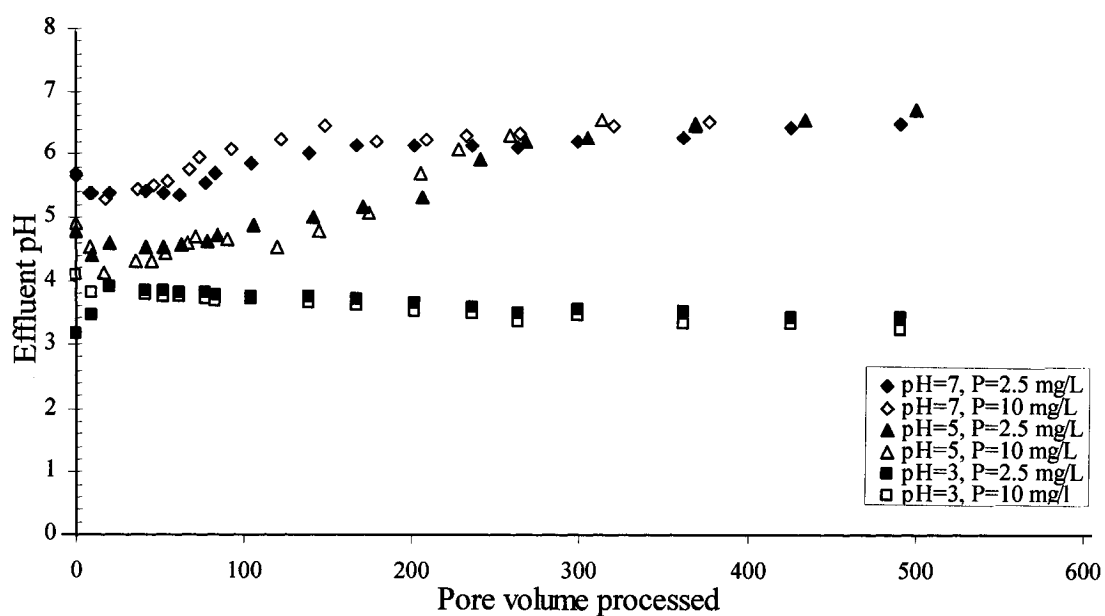
Figure 7-9. Effect of influent pH and initial phosphorus concentration on the effluent pH

7.4 Application of Oven Dried Alum Sludge Adsorbents to Wastewater

7.4.1 Treatment of secondary municipal effluent

Experiments conducted on the secondary municipal effluent showed that oven dried alum sludge were effective in removing phosphorus from secondary municipal effluent (Figure 7-10). However, the breakthrough pore volumes were lower than that of deionized water spiked with orthophosphates. This was probably due to the presence of other contaminants in wastewater that might compete for adsorption sites. Breakthrough pore volumes for orthophosphates were consistently higher than that of total phosphorus (Table 7-4). This was indicative of oven dried alum sludge being more effective in adsorbing orthophosphates than any other species of phosphorus. Wastewater pH of 5 appeared to have the highest adsorption of orthophosphates and total phosphorus. However, changes in pH to 3 or 7 decreased the adsorption of total phosphorus. This finding was consistent with the results found in deionized water.
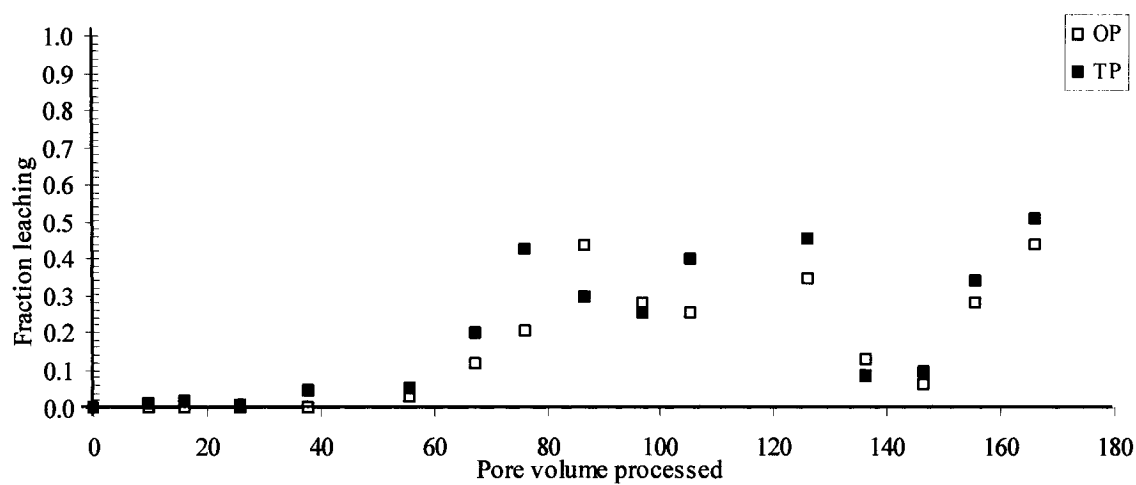
a) pH = 3
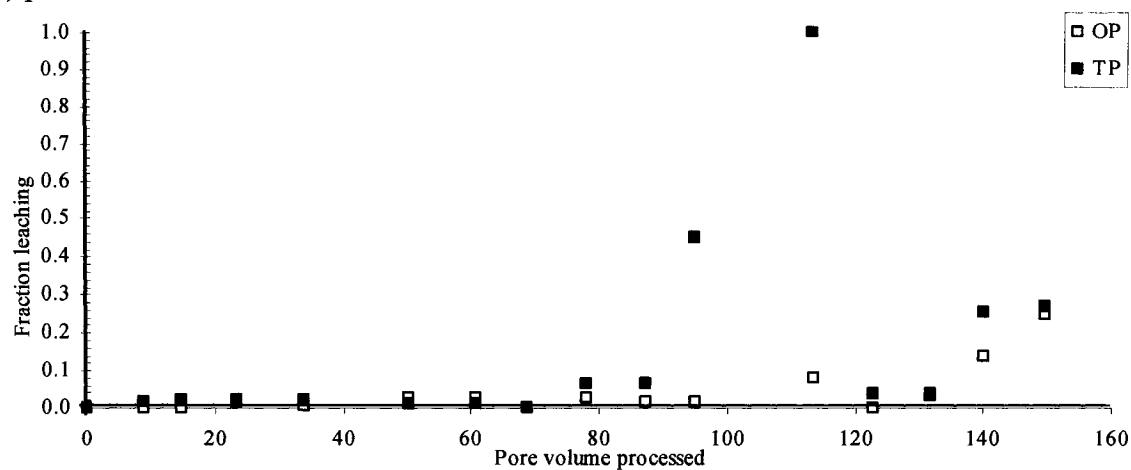
b) pH = 5
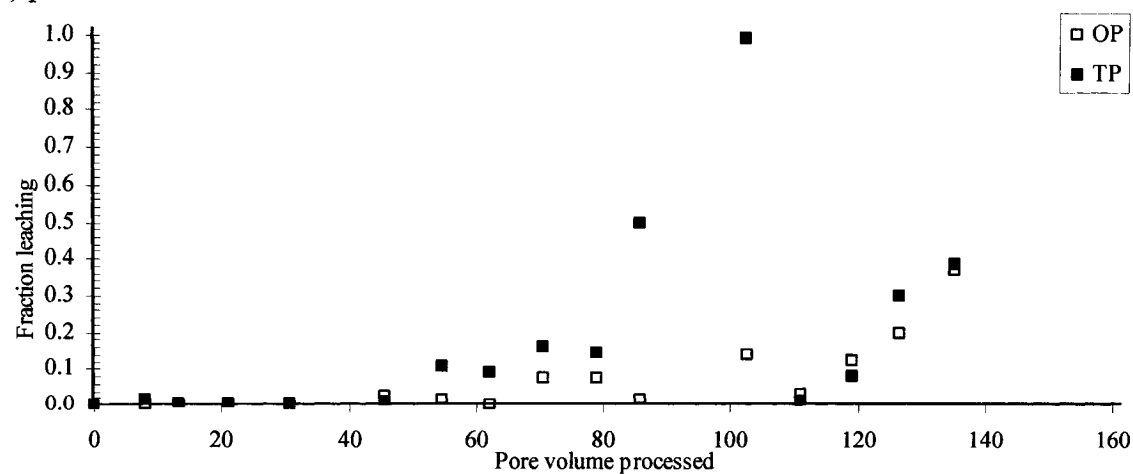
c) pH = 7

Figure 7-10. Phosphorus removal with secondary municipal effluent

Table 7-4. Summary of breakthrough pore volumes in fixed bed column tests

Wastewater	Secondary municipal			Pilot scale biofiltration		Bench scale biofiltration		Aquaculture process water		
pH	3	5	7	6.5	5	Col. 1	Col. 2	3	5	7
Orthophosphate	67	114	71	140	159	462	270	610	659	640
Total phosphorus	67	78	55	140	103	336	193	138	150	145

The effluent pH levels were in the range of 5.5-7.5 for an influent pH of 5 and 7 (Figure 7-11). However, for an influent pH of 3, effluent pHs were within the range of 3-4. These pHs were similar in values to the pHs observed during batch adsorption experiments. The effluent pH values for both the influent pH of 5 and 7 were mostly suitable for disposal in surface waters with little or no addition of lime.
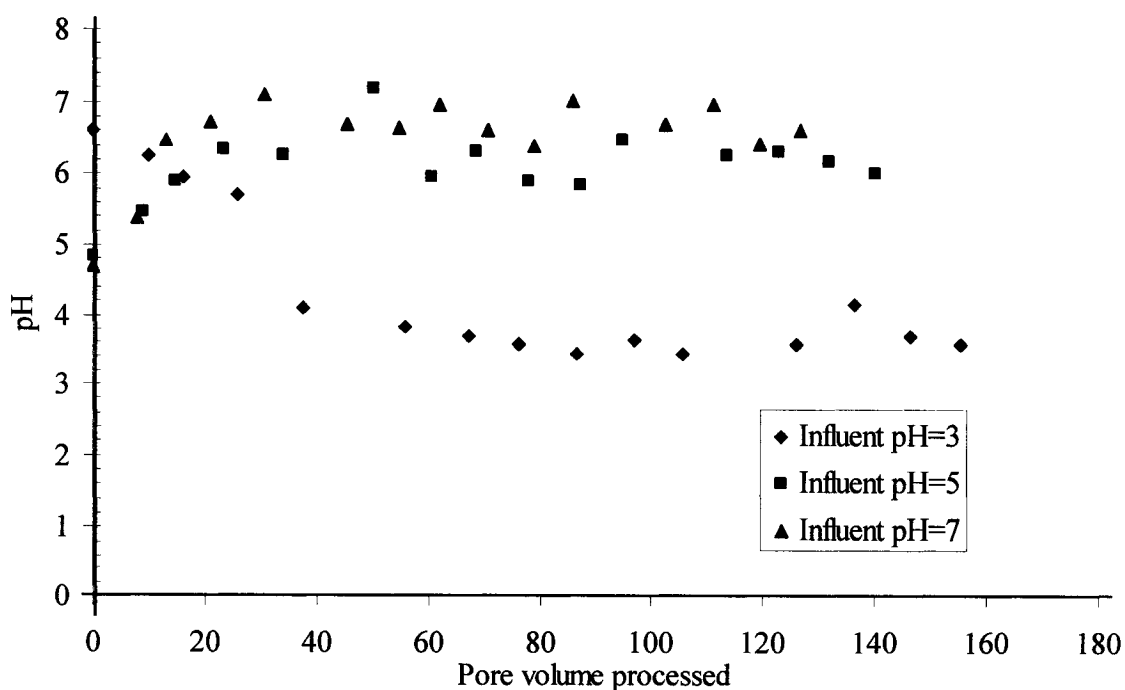
Figure 7-11. Effluent pH at various pore volumes processed for secondary municipal effluent

Aluminum leaching was in general, high (> 1 mg/L) in the beginning of the experiments

for both pH of 5 and 7 (Figure 7-12). However, over time, aluminum leaching decreased

to less than 0.2 mg/L. In many cases, the effluent aluminum concentrations were even

lower than the raw water aluminum concentrations. It implied that oven dried alum

sludge was able to absorb aluminum from the raw water. Aluminum leaching for a pH of

3 was consistently high all over the experiments, except after processing a pore volume

of 100, the leaching of aluminum decreased. It was understandable as acidic environment

entices metal leaching. This result was also consistent with the findings in deionized

water.
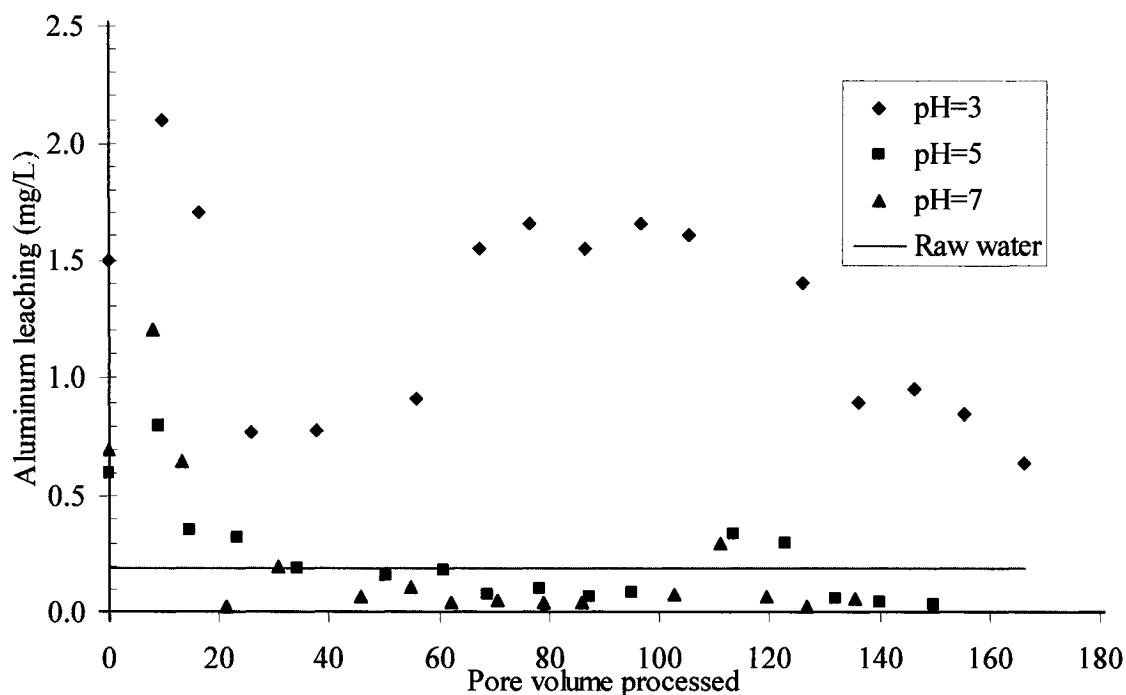
Figure 7-12. Effluent aluminum concentrations at various pore volumes processed for

secondary municipal effluent

BOD$_5$ values were in general, lower in the samples tested than the raw water (average

obtained from testing five times at equal interval throughout the testing period) (Figure 7-

13). It implied that oven dried alum sludge was able to adsorb organic matter from the

raw water. There were no definite patterns for organic leaching. As the organic leaching

pattern cannot be correlated with phosphorus leaching behavior, it can be fairly assumed

that organic matter did not compete for adsorption sites with phosphate. It was consistent

from previous findings. BOD$_5$ values in most of the experiments were less than 30 mg/L.

It indicated that the wastewater after adsorption of phosphorus in oven dried alum sludge

was safe for disposal in surface water. Changes in pH did not seem to affect organic

leaching considerably.
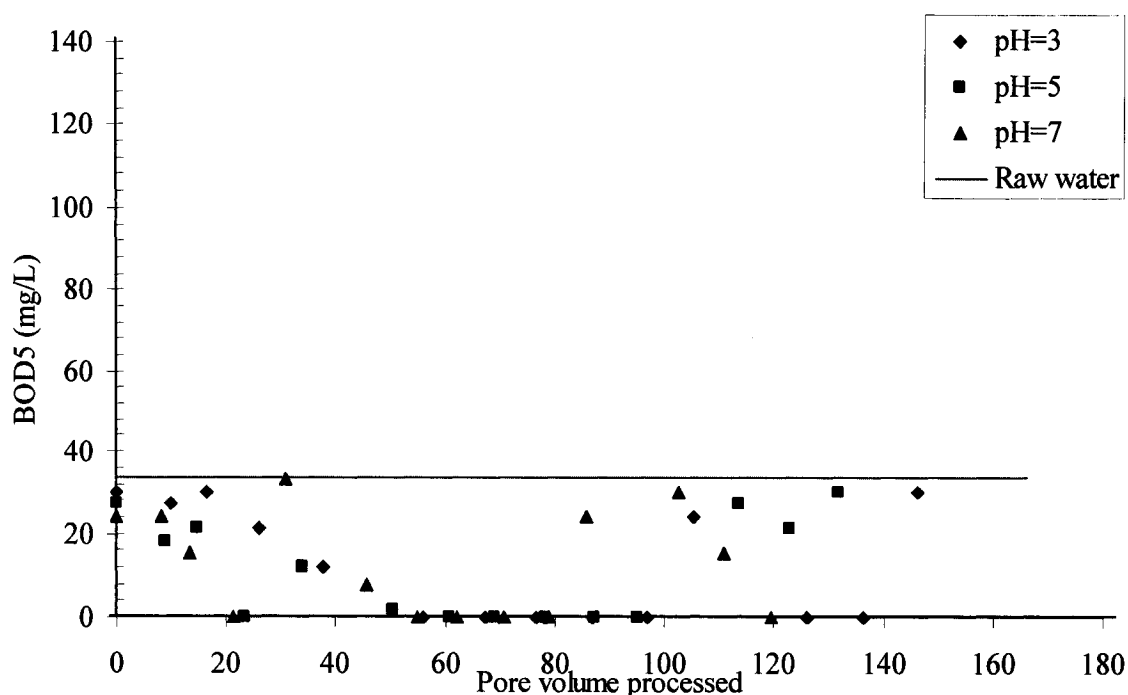
Figure 7-13. Effluent BOD$_5$ at various pore volumes processed for secondary municipal effluent

7.4.2 Treatment of on-site decentralized wastewater

Experimental results showed that oven dried alum sludge was effective in removing phosphorus from biofiltration wastewater (Figure 7-14). Phosphorus leaching broke through after processing 103-159 pore volumes of pilot scale biofiltration wastewater (Table 7-4). Experiments conducted with bench scale wastewater also showed effective phosphorus adsorption in oven dried alum sludge. However, phosphorus removals were more effective with bench scale biofiltration wastewater than pilot scale biofiltration wastewater. This was consistent with the findings from batch adsorption tests. Oven dried alum sludge was effective in removing phosphorus even up to 462 pore volumes of bench scale biofiltration wastewater processed. It was higher than that of pilot scale biofiltration wastewater. Phosphorus removals were higher for orthophosphates than for total phosphorus, supported by larger breakthrough pore volumes in orthophosphates than total phosphorus. This was consistent with the findings from treatment of secondary municipal effluent. Wastewater pH of 5 appeared to have higher adsorption of orthophosphates than the pH level of 6.5 in pilot scale biofiltration wastewater. However, an influent pH of 6.5 had a higher breakthrough pore volume than pH level 5 for total phosphorus. Breakthrough pore volumes were higher than that of deionized water, though experiments were conducted at identical environmental conditions.
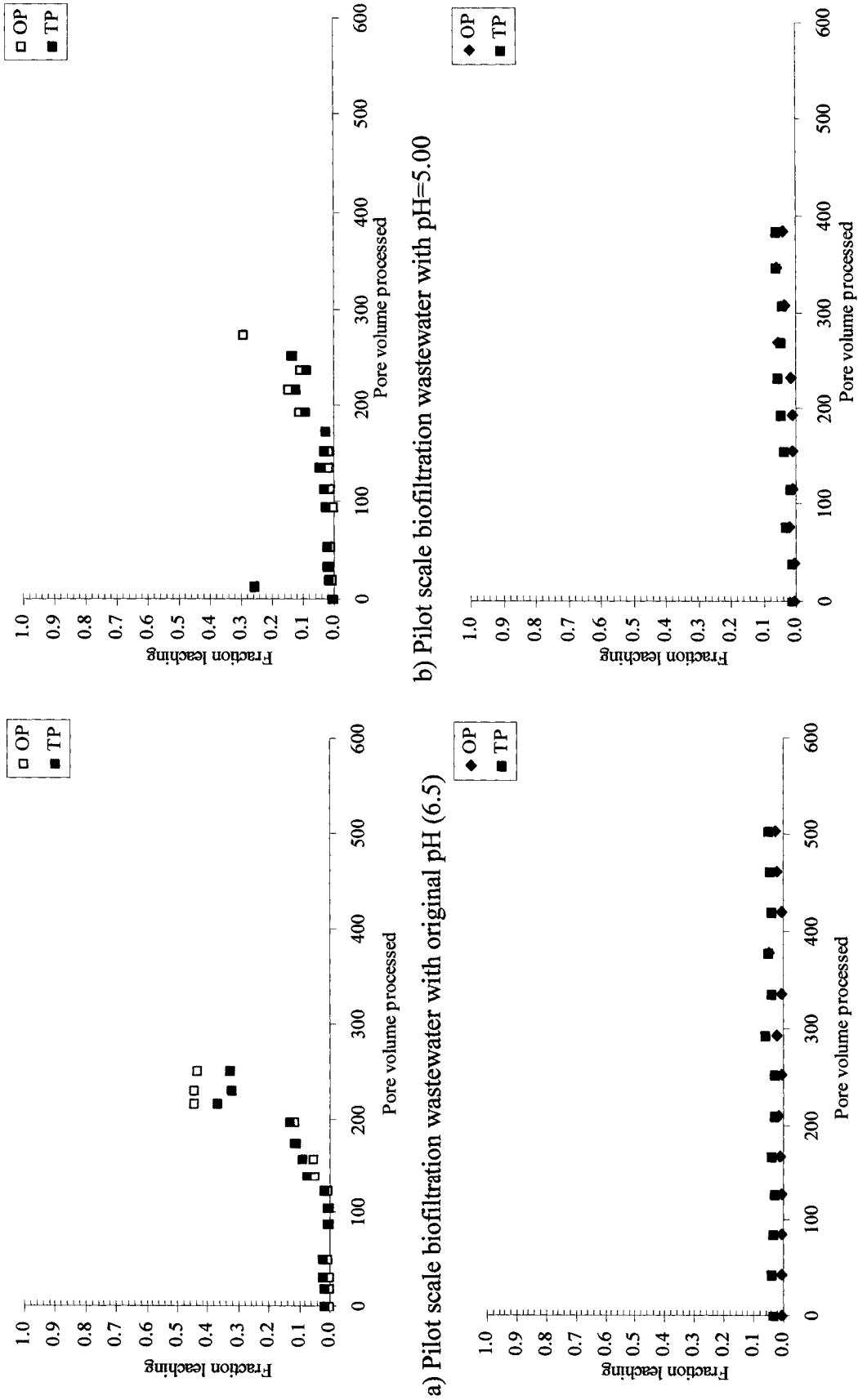
a) Pilot scale biofiltration wastewater with original pH (6.5)

b) Pilot scale biofiltration wastewater with pH=5.00

c) Bench scale biofiltration wastewater (sample 1)

d) Bench scale biofiltration wastewater (sample 2)

Figure 7-14. Phosphorus removal in fixed bed column tests for effluent from biofilter

The effluent pH levels ranges within 6-7.5 for most of the samples tested (Figure 7-15).

For both types of biofiltration wastewater used in this research, pH did not vary much.

These pH values were higher in values than the pH values observed during batch

adsorption experiments. These pH values were suitable for disposal in surface waters.

Aluminum leaching was in general, high in the beginning of the experiments (Figure 7-16). However, over time, aluminum leaching decreased. Aluminum leaching behaviour

was consistent in both types of wastewaters. In many cases, aluminum concentrations

were lower than the concentration present in the raw water. It indicated that oven dried

alum sludge absorbed aluminum in those cases. Low pH (pH=5) in pilot scale

biofiltration wastewater was shown to have lower leachability in the beginning of the
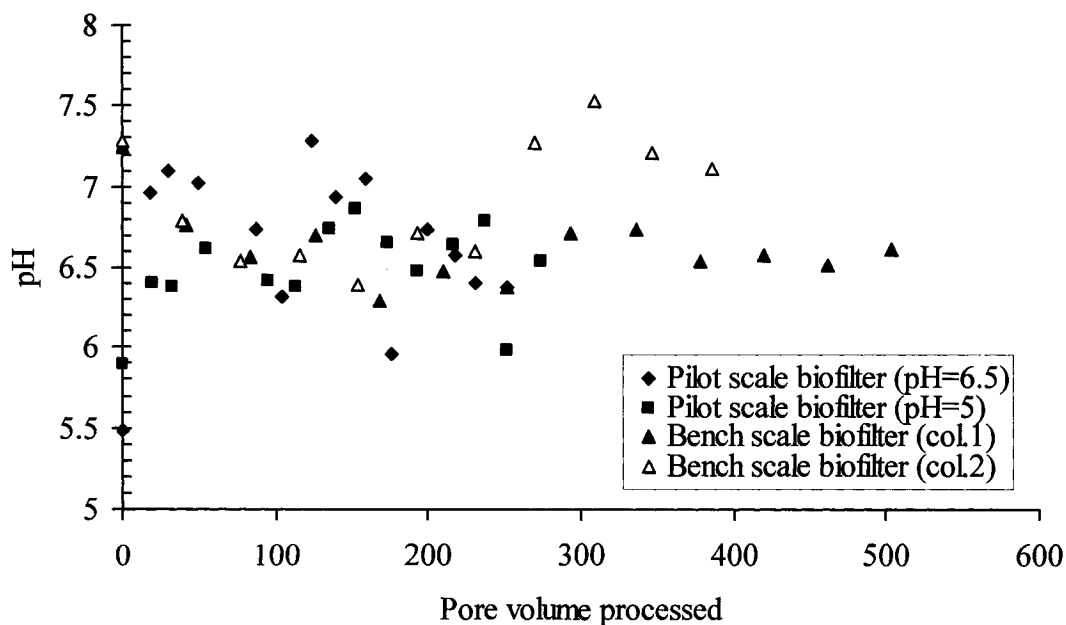
Figure 7-15. Effluent pH at fixed bed column tests for biofiltration wastewater

experiments. However, later in the experiment, the leaching was consistently higher than wastewater having a higher pH (6.5). Experiments conducted with bench scale biofiltration wastewater also showed that aluminum leaching was lower than raw water in most of the samples tested.

The effluent BOD_5 values were in general, lower in most of the samples tested than the raw water (Figure 7-16). However, organic leaching was higher in pilot scale biofiltration wastewater than bench scale biofiltration wastewater. This was because of the high BOD_5 values of raw water. It indicated adsorption of organic matter in pilot scale biofiltration wastewater. BOD_5 values in most of the experiments were less 30 mg/L. It indicated that the wastewater after adsorption of phosphorus in oven dried alum sludge was safe for disposal in surface water. Changes in pH values in pilot scale biofiltration wastewater did not seem to affect organic leaching considerably.
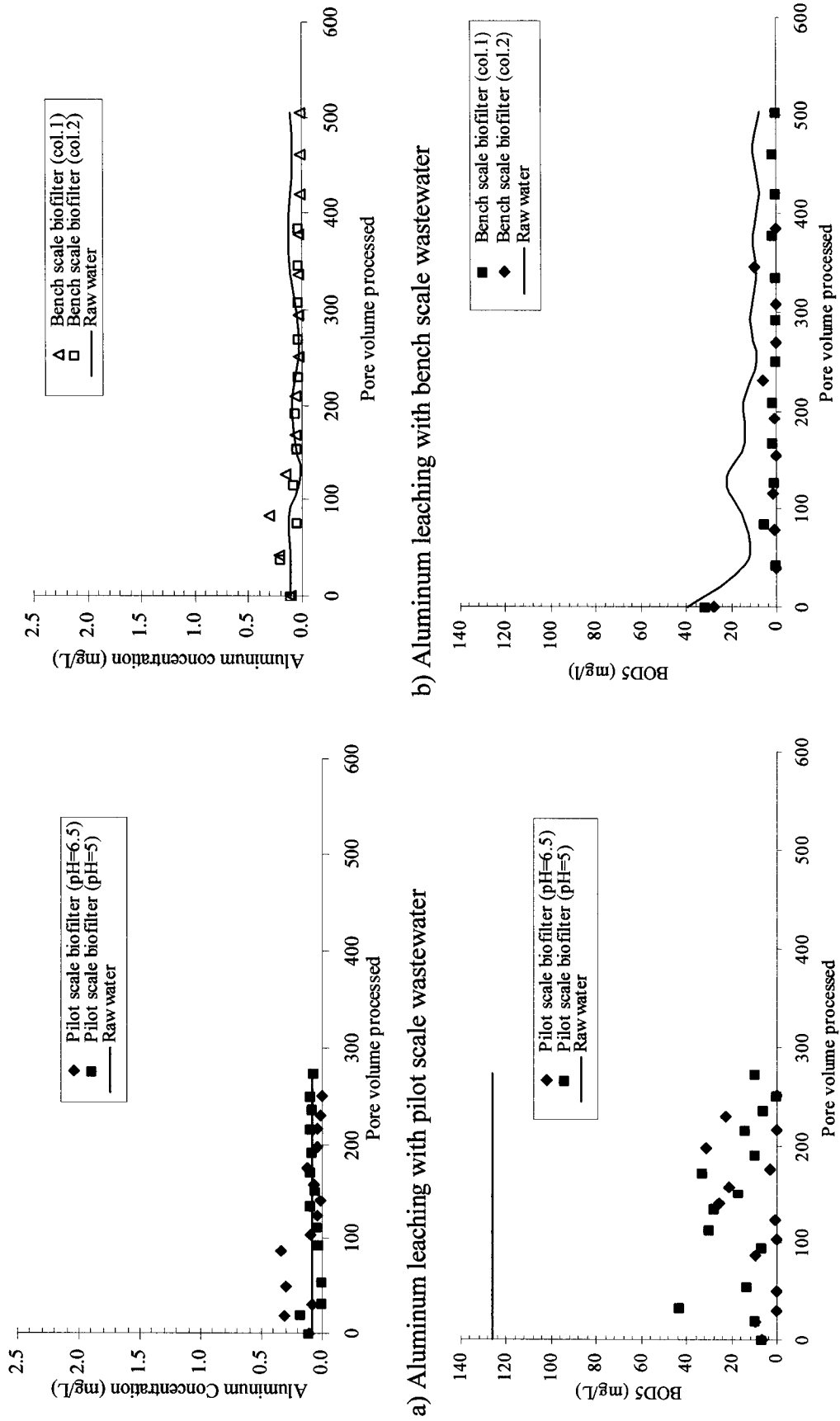
a) Aluminum leaching with pilot scale wastewater

b) Aluminum leaching with bench scale wastewater

c) BOD₅ leaching with pilot scale wastewater

d) BOD₅ leaching with bench scale wastewater

Figure 7-16. Leaching of other contaminants for biofiltration wastewater

7.4.3 Treatment of aquaculture process water

Fixed bed column test results showed that oven dried alum sludge was effective in removing phosphorus from aquaculture process water (Figure 7-17). Phosphorus leaching broke through 610-659 pore volumes of the column used for orthophosphates (Table 7-4). The breakthrough for total phosphorus occurred at pore volumes of 138 to 150. It was consistent with results from other types of wastewater. It was also consistent with the findings from the batch tests. Wastewater pH did not show any considerable effect on the orthophosphate and total phosphorus removal of alum sludge. The breakthrough pore volumes were higher than that of deionized water and other small-scale wastewaters treated. It was due to the low initial phosphorus concentrations observed in aquaculture water.

The effluent pH was in the range of 4-6 in the beginning of the experiment (Figure 7-18). However, in the course of the experiment, effluent of the raw water pH of 3 decreased further. The effluent for a pH of the raw water pH of 5 varied in the range of 4.5-6. However, the effluent pH of the raw water pH of 7 varied in the range of 6-7. The experimental results indicated that operating raw water at a pH of 7 would be suitable for disposal of the effluent in surface water. However, treatment can allow variation in raw water pH, as the differences in pH did not affect the phosphorus adsorption much.
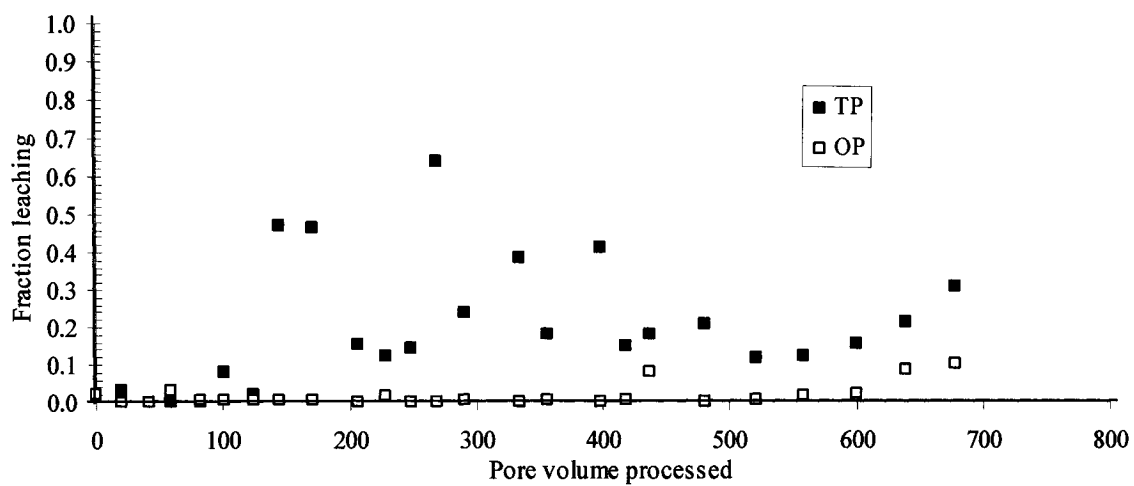
a) pH = 7
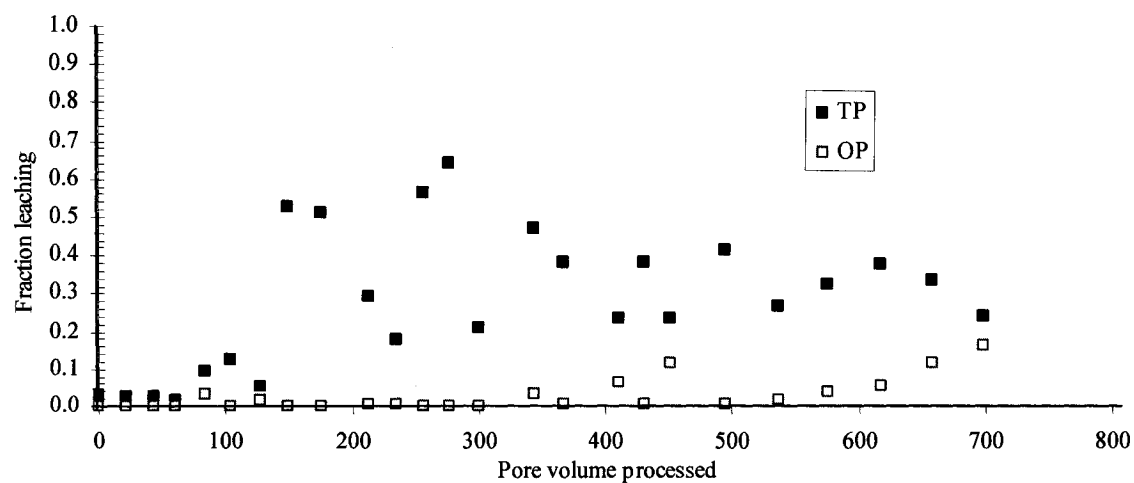
b) pH = 5
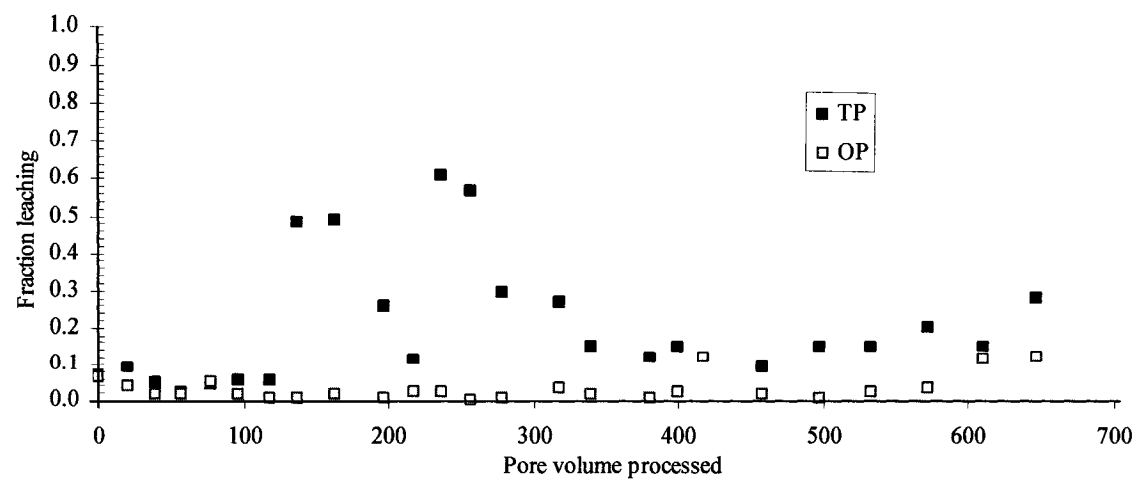
c) pH = 3

Figure 7-17. Phosphorus removal in column tests with aquaculture water
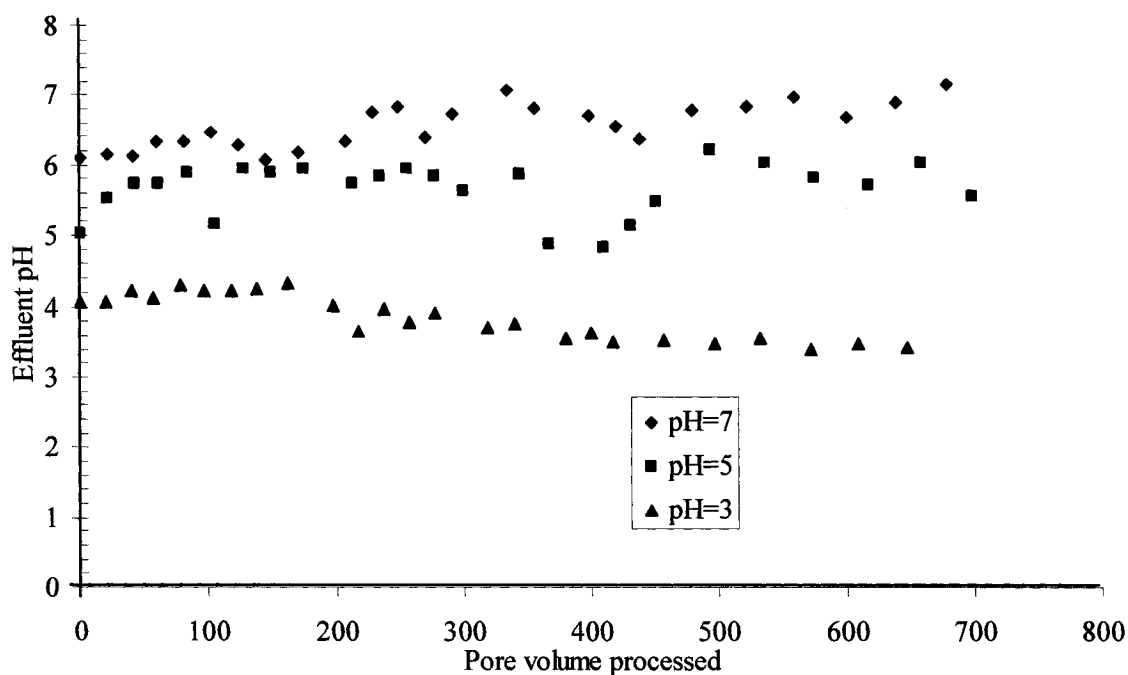
Figure 7-18. Effluent pH after treatment of aquaculture process water

The leaching of aluminum was observed to be mostly below 0.5 mg/L (Figure 7-19).

Aluminum leaching was consistently high in the beginning of the experiment. However,

in the course of the experiment, aluminum leaching lowered. Aluminum leaching was

observed to be high for a pH of 3. The leaching was the lowest at a pH of 5. Aluminum

leaching was however consistently higher than the aluminum concentration in the raw

water. It implied that aluminum in the effluent was a contribution from oven dried alum
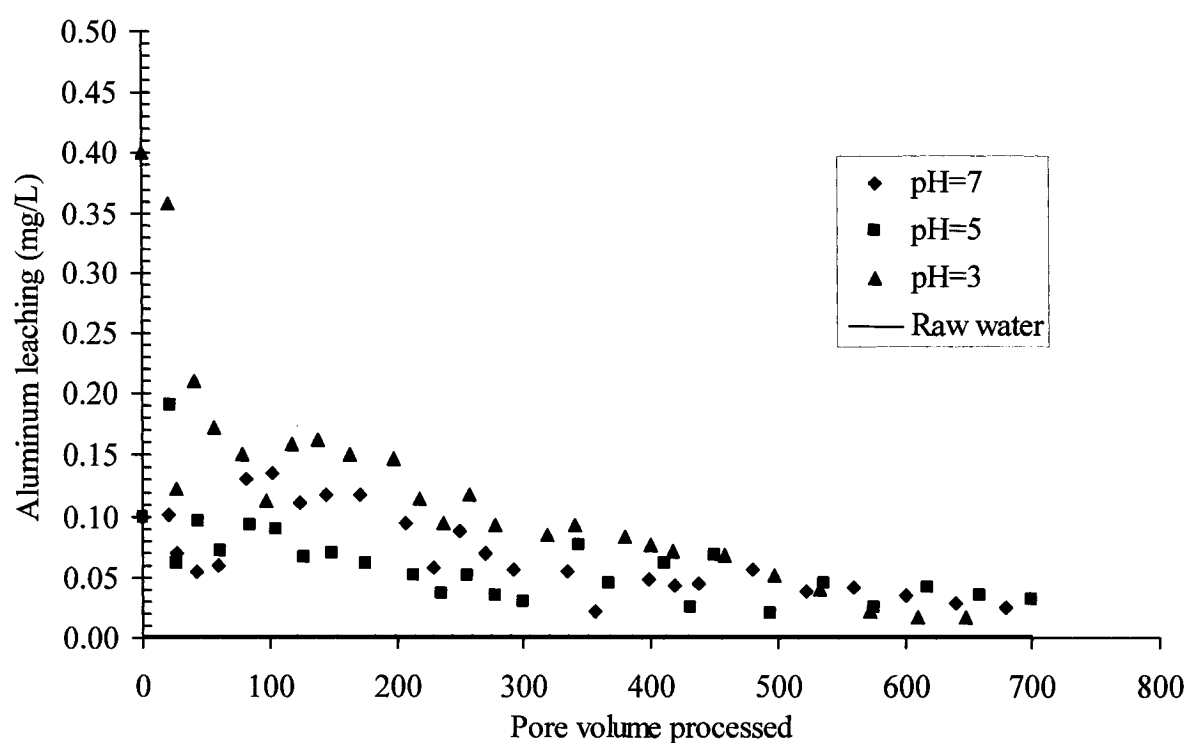
sludge.

Figure 7-19. Aluminum leaching after treatment of aquaculture water

There was adsorption of organic matter onto oven dried alum sludge as the raw water

BOD_5 was higher than the effluent BOD_5 values of fixed bed column tests (Figure 7-20).

There was a considerable decrease in adsorption of organic matter in the pore volume of

300-400. BOD_5 of the effluent was mostly lower than 30 mg/L. There was an increase in

BOD_5 (>30 mg/L) during the processing of 300-400 pore volumes. It indicated that the

effluent generated after removing of phosphorus would be mostly suitable for disposal in

surface water. The pH of the raw water did not affect the adsorption of organic matter

considerably.
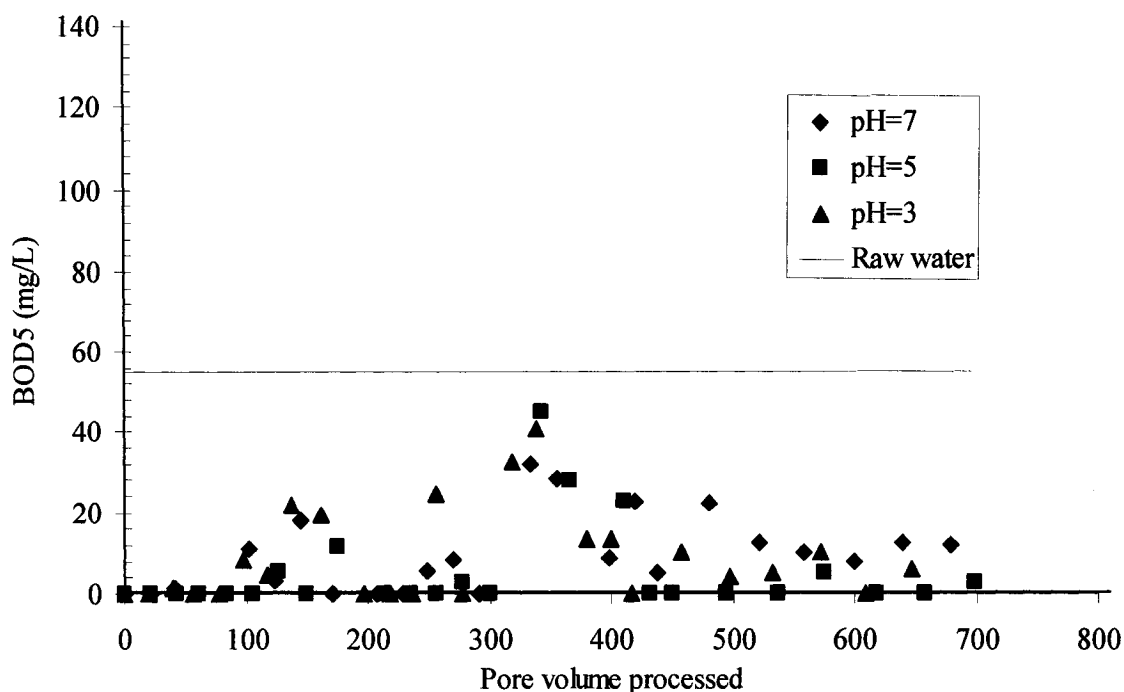
Figure 7-20. Organic content leaching after treatment of aquaculture water

7.5 Conclusions

The fixed bed column tests were shown to be reproducible. The phosphorus removal

capability of oven dried alum sludge was comparable to granular activated carbon. Blast

furnace slag had the best phosphorus removal capability among the materials tested.

However, the effluent pH of more than 10 for blast furnace slag was not suitable for

disposal in surface water. Fine particle sizes had better adsorption of phosphorus than

coarse particles. However, fine particles had high aluminum leaching compared to coarse

particles. The leaching of organic matter was not affected by the particle size. A pH of 3

consistently removed phosphorus from water. However, water with a pH of 5 seemed to

have larger breakthrough pore volumes than other pH values. It was supported by

ANOVA test for 2.5 mg/L of phosphorus inflow. However, the effect of pH in these

studies was based on deionized water. The leaching of aluminum was high at a pH of 3.

However, aluminum leaching for other pH levels was not that high. Influent pH levels conceivably affected the effluent pH levels. Initial phosphorus concentrations affected the phosphorus removal behaviour. High initial phosphorus concentrations had smaller breakthrough pore volume than low initial phosphorus concentrations. There were no effect of initial phosphorus concentration on aluminum and organic matter leaching and effluent pH levels.

Oven dried alum sludge also appeared to effectively remove phosphorus from small-scale wastewater applications. The phosphorus removal capability of oven dried alum sludge from small-scale wastewater was comparable and even better than phosphorus removal from deionized water. The phosphorus removal varied with the variability in wastewater characteristics. The removal of total phosphorus was not as effective as the removal of orthophosphates. The effluent pH levels were mostly suitable for disposal in surface water without any pH treatment.

8.0 APPROPRIATE UNIT OPERATION FOR ALUM RESIDUALS: ADSORPTION VERSUS COAGULATION

8.1 Introduction

Both adsorption and coagulation are the most efficient physical chemical treatment alternate for removal of phosphorus, as shown in Chapter 3. The objective of this chapter was to evaluate the efficiency of phosphorus removal by using coagulation followed by flocculation and sedimentation as a process alternate. This chapter also examines the effect of pH, coagulant concentration, wastewater characteristics on the phosphorus removal efficiency in coagulation process. Comparative advantages and disadvantages are discussed between adsorption and coagulation as a process alternate for phosphorus removal from small-scale wastewater.

8.2 Experimental Procedure

Alum sludge and oven dried alum sludge were compared to conventional coagulant alum and limestone at a coagulant concentration of 1 g/L. The particle sizes for the oven dried alum sludge and limestone were used to be less than 250 µm. The particle sizes of alum and raw alum sludge were not known as they were used as dissolved and semisolid respectively. Municipal wastewater from Millcove Water Pollution Control Plant, Nova Scotia was used for the experiments. Oven dried alum sludge was used for further studies, as coagulation would be compared to similar studies for adsorption as a process alternate. Two different types of small-scale wastewater were used; the same municipal wastewater and aquaculture water. The effect of pH was evaluated for three different pH

levels 3, 5 and 7 at an oven dried alum sludge concentration of 1.5 g/L on municipal
wastewater.

Reproducibility of the experimental setup was determined using six sets of data for
samples at three different alum concentrations including a blank. As coagulation is
generally used as a technology for particulate removal, municipal wastewater from
Millcove Water Pollution Control Plant, Nova Scotia was used for this test.
Environmental conditions were set identical.

8.3 Results on Coagulation as Phosphorus Removal Alternate

8.3.1 Reproducibility

The experimental setup was shown to produce reproducible results (Figure 8-1). Standard
deviations ranged from 0.17 to 0.19 for an average orthophosphate (OP) concentration of
1.03 to 3.48 mg/L, from 0.1 to 0.27 for average total phosphorus (TP) concentration of
1.23 to 6.05 mg/L and from 0.05 to 0.17 for average particulate phosphorus (PP)
concentration of 0.2 to 2 mg/L.
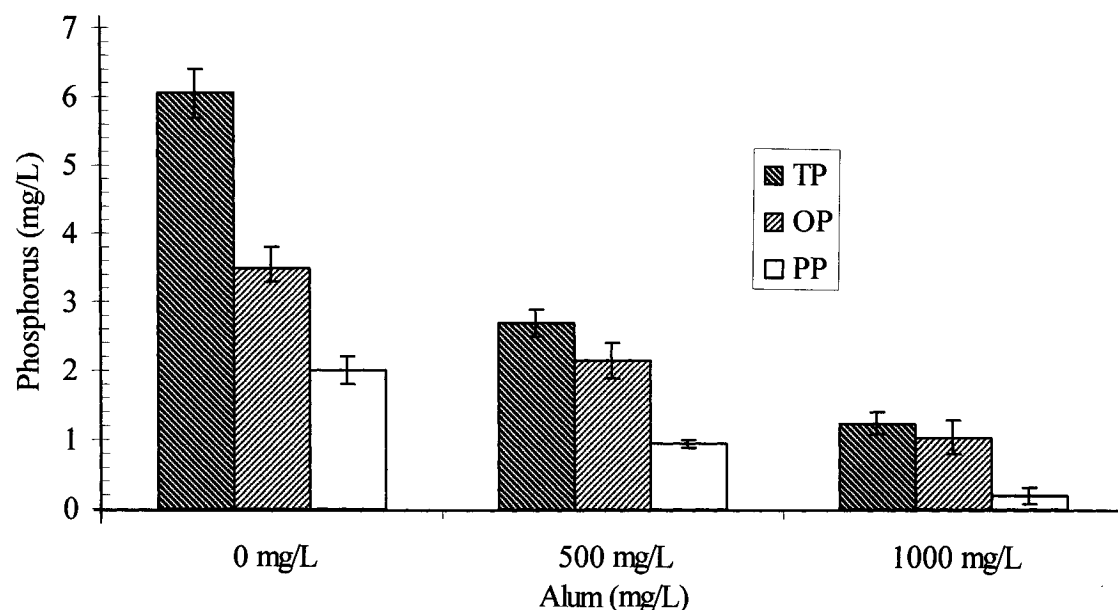
Figure 8-1. Reproducibility of experimental results from jar tests

8.3.2 Different types of alum sludge compared to conventional coagulant

Experimental results showed that phosphorus removal efficiencies from raw alum sludge

and oven dried alum sludge were not comparable to conventional coagulant alum (Figure

8-2). For a coagulant concentration of 1 g/L, removal of different species of phosphorus

varied from 7%-26% for alum sludge and 7%-31% for oven dried alum sludge. Lower

coagulant concentrations for alum sludge were also not effective for removal of

phosphorus. Even the particulate phosphorus was not removed using alum sludge as a

coagulant. Preliminary experiments conducted with deionized spiked with

orthophosphate as in the previous chapters also did not show considerable phosphorus

removal using alum sludge. The results were not consistent with the findings from a

previous study (Baldwin et al., 1974). However, the composition and characteristics of

alum sludge may not be the same, as it was a product of raw water characteristics,

chemicals added and treatment options used in the water treatment plant, where the alum

sludge was generated. Alum was the best coagulant for removal of phosphorus among the

coagulants tested. This was also consistent with previous studies (Sherman et al., 2000;

Aguilar et al., 2002). Limestone was not effective in removing phosphorus from

municipal wastewater.
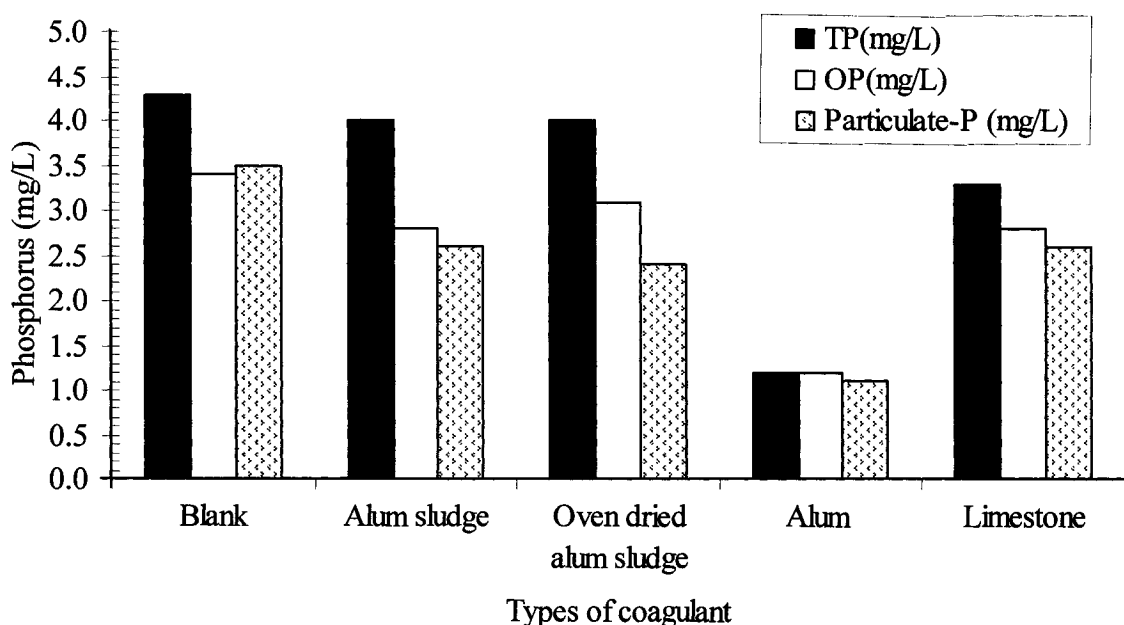
Figure 8-2. Effluent phosphorus concentration with different coagulants

Effluent pH values did not change for raw and oven dried alum sludge and limestone

(Figure 8-3). However, effluent pH for alum was dropped to less than 4 from an influent

pH of higher than 6. Turbidity as observed after the experiments did not change much

(Figure 8-3). Raw alum sludge and alum was able to reduce the turbidity of the raw

water. However, oven dried alum sludge and limestone increased the turbidity. This was

probably because these coagulants have large amount of fine particles that did not settle during the course of the experiments.
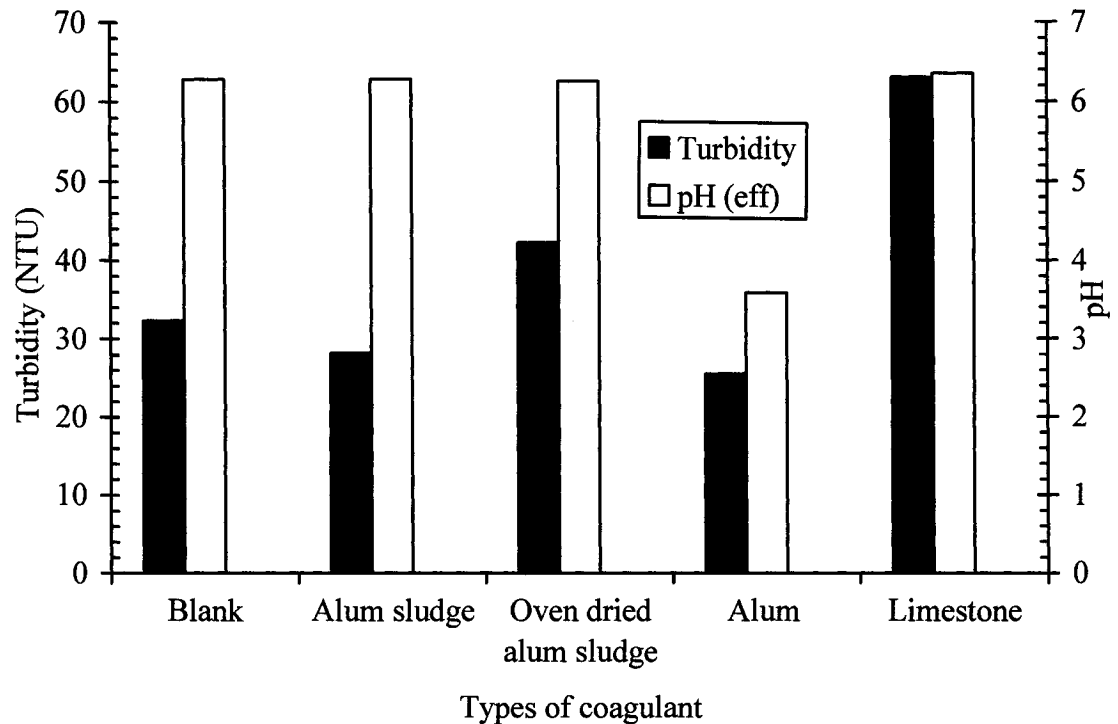
Figure 8-3. Effluent pH and turbidity with different coagulants

8.3.3 Phosphorus removal from small-scale wastewater

Experimental results showed that oven dried alum sludge were not very effective in removing different types of phosphorus present in both municipal and aquaculture wastewater (Figure 8-4). It was probably because oven dried alum sludge could not coagulate, flocculate or even adsorb within the timeframe of the experiments conducted. Increase in coagulant concentration also could not increase the phosphorus removal efficiencies considerably. However, coagulant concentration over 1 g/L would produce excessive sludge; thereby would be unrealistic as a commercial application.
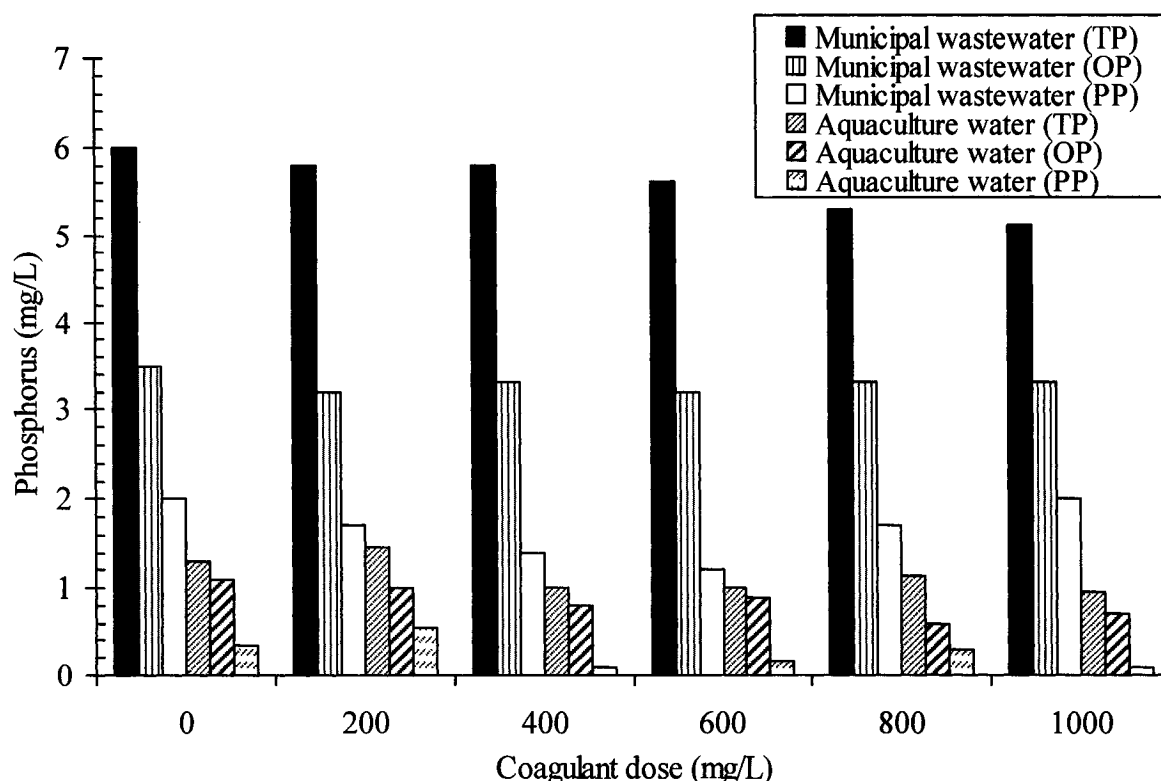
Figure 8-4. Effluent phosphorus concentration of small-scale wastewater applications

Effluent pH did not change after the experiments for both types of wastewater (Figure 8-5). pH was not affected considerably with the increasing oven dried alum sludge concentrations. The pH values were mostly within 6-8. These pH values were suitable for disposal in surface water. Turbidity of municipal wastewater during increasing oven dried alum sludge concentrations decreased initially, then increased afterwards (Figure 8-5). This was because oven dried alum sludge was removing some of the colloidal particulates that were creating the turbidity. However, with additional oven dried alum sludge, turbidity increased due to the oven dried alum sludge itself. However, as aquaculture water did not have a high turbidity, the values of turbidity increased continuously with increasing oven dried alum sludge concentrations. The fine oven dried alum sludge particles were suspended and contributed to the additional turbidity.
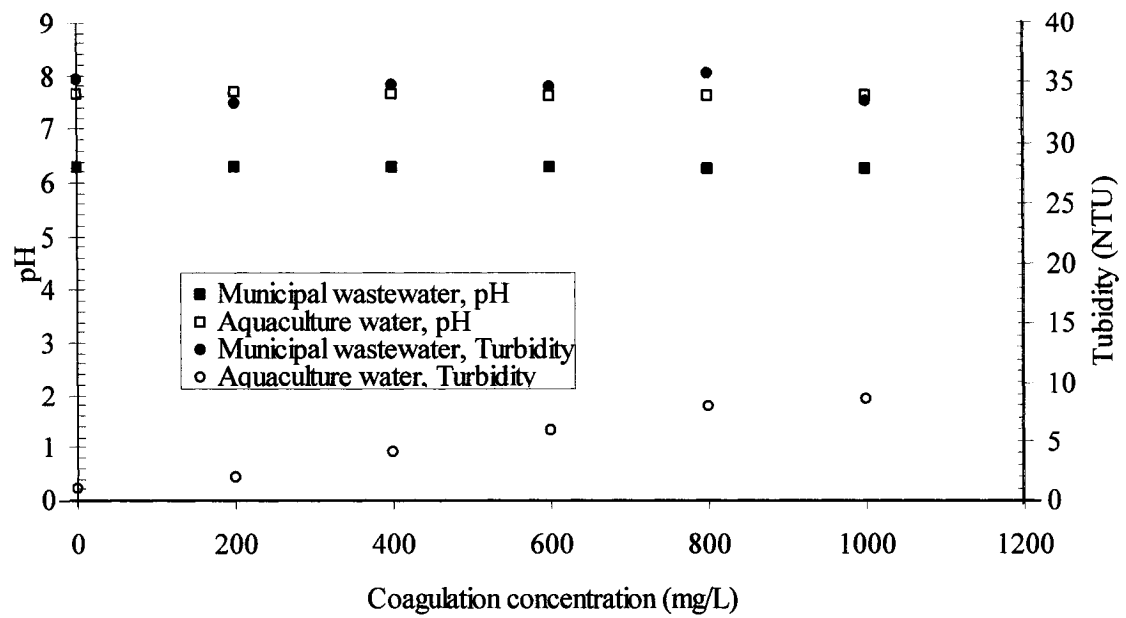
Figure 8-5. pH and turbidity of small-scale wastewater experiments

The sludge (as represented by total suspended solids) generated in the process of the

coagulation followed by flocculation and sedimentation increased with the increase in

oven dried alum sludge concentrations (Figure 8-6). It implied that higher concentrations

of oven dried alum sludge as a coagulant was not only ineffective in removing

phosphorus, but also produced a large amount of solids in the sludge. Both of these issues

would be undesirable for wastewater treatment.
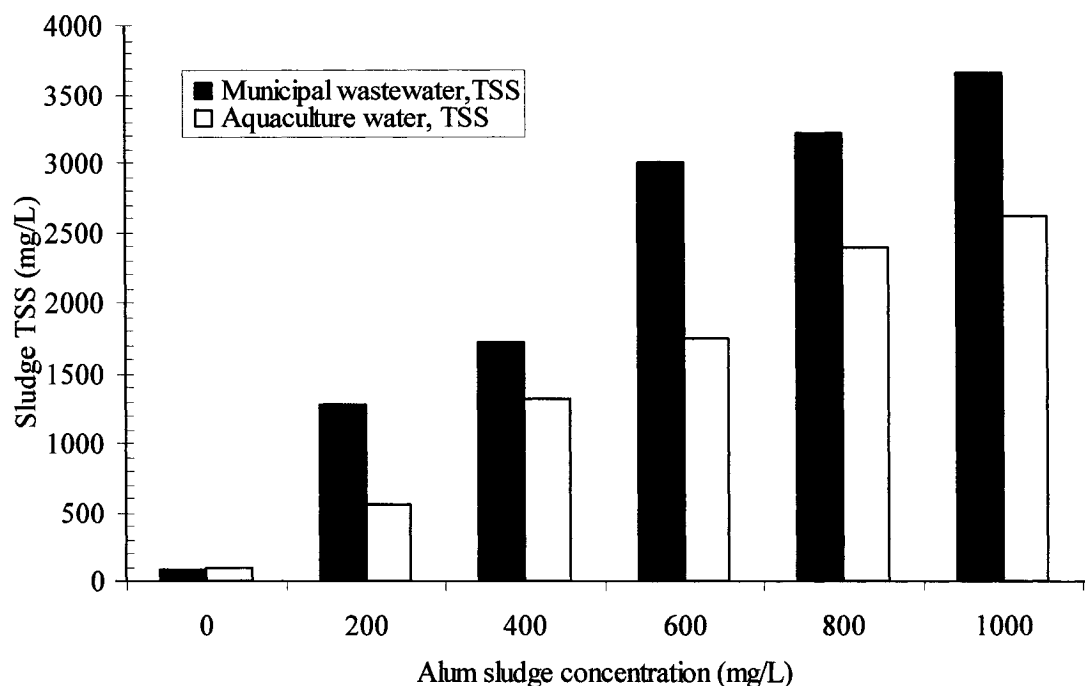
Figure 8-6. Sludge total suspended solids of small-scale wastewater experiments

8.3.4 Effect of pH

Changes in pH as evidenced from the experimental results had no considerable effect on the effluent phosphorus concentrations (Figure 8-7). A pH of 7 had the highest phosphorus removal and a decrease in pH from that decreased the phosphorus removal and increase the effluent phosphorus level. However, the differences in orthophosphate and particulate phosphorus were not considerable. The maximum decrease in total phosphorus removal of 16% occurred with a pH drop from 7 to 5.
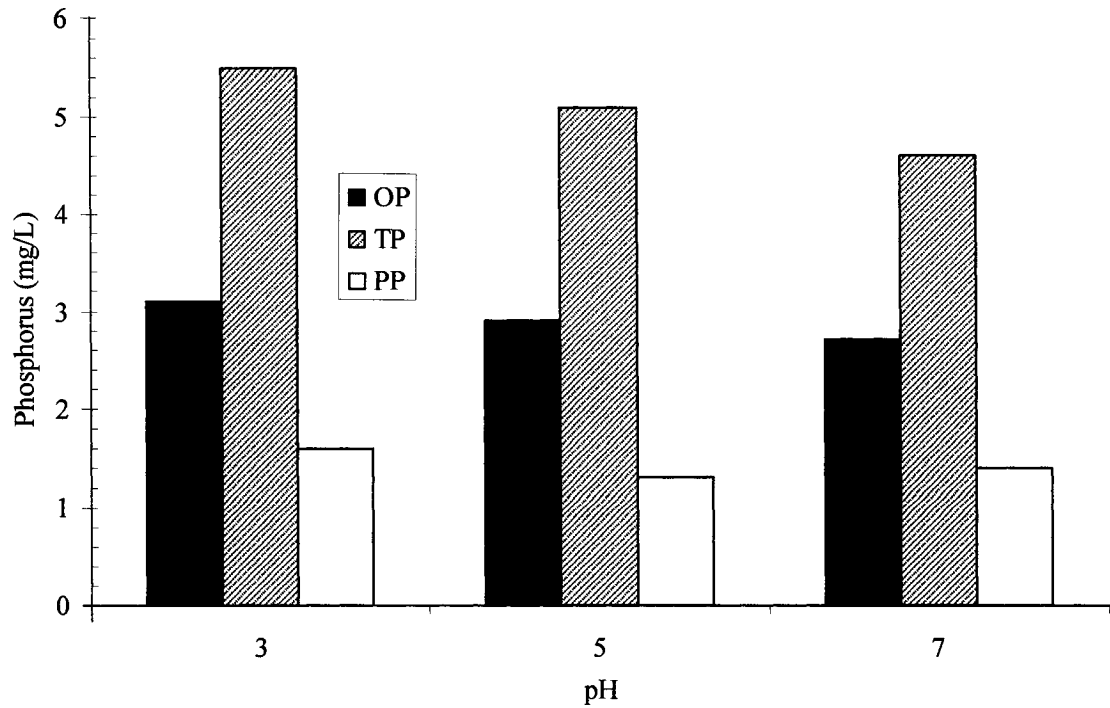
Figure 8-7. Effect of pH on the effluent phosphorus concentrations

Experimental results showed that turbidity increased with a decrease in pH from a maximum tested pH of 7 (Figure 8-8). This was probably because a decrease in effluent concentration caused by sedimentation. The maximum sludge solids content was for a pH of 7 and the sludge solids decreased with a decrease in pH (Figure 8-8). It also supported the idea that solids settled more at a pH 7 than at other pHs. However, the differences were small.
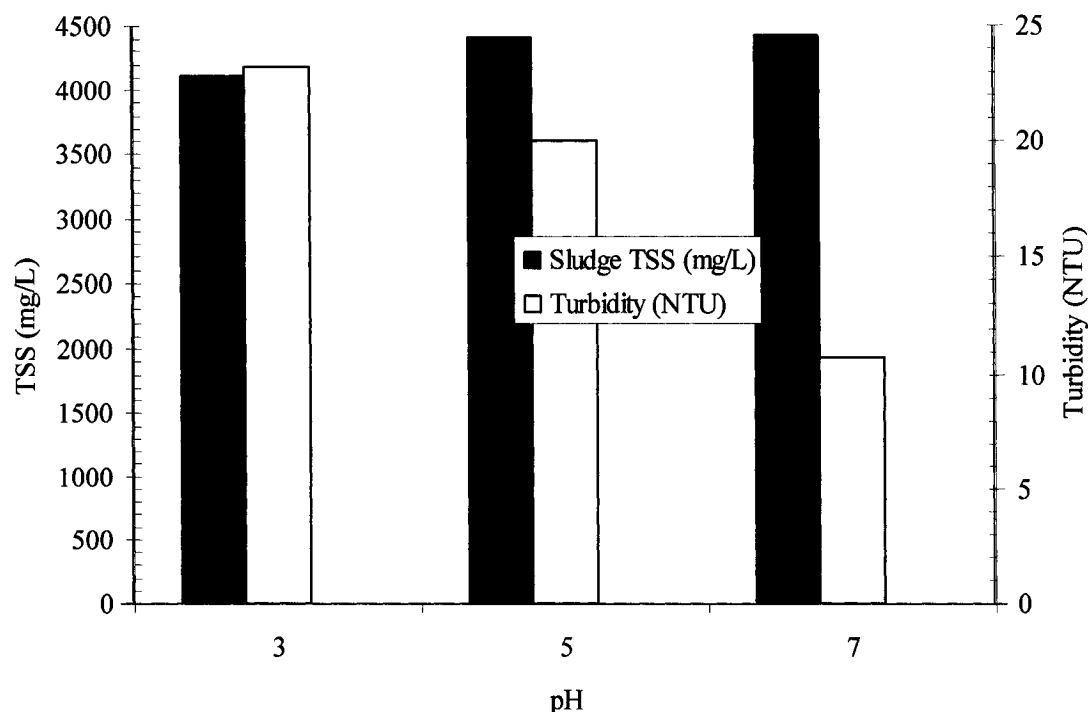
Figure 8-8. Effect of pH on turbidity and sludge total suspended solids

8.4 Comparative Analysis of Adsorption versus Coagulation

8.4.1 Phosphorus removal efficiency

Oven dried alum sludge was shown to be effective as an adsorbent for phosphorus

removal (Table 8-1). However, unlike previous studies coagulation did not seem to be

effective for removal of orthophosphate. This was probably due slow adsorption process.

The removal of phosphorus using coagulation was done through adsorption of

phosphorus onto dried alum sludge. However, due to low contact time (91 minutes), the

coagulation process was not successful. On the contrary, the adsorption process took into

account the time needed (12 days) for the possible maximum adsorption onto oven dried

alum sludge. Changes in pH and initial phosphorus did not improve the phosphorus

removal efficiencies in the coagulation process much. Therefore, adsorption was found to be more effective as a treatment process alternate than coagulation.

Table 8-1. Comparative orthophosphate removal efficiency between adsorption and coagulation of oven dried sludge

Type of wastewater	Particle size (μm)	Initial P* (mg/L)	Alum sludge (g/L)	pH	Adsorption (%)	Coagulation (%)
Municipal	<250	3-4	1 1.5 1.5 1.5	6 3 5 7	83 90 93 88	6 9 15 21
Aquaculture water	<250	1.1	1	7	93	36

* P = orthophosphate-P

8.4.2 Other relevant aspects

Appropriate technology for small-scale wastewater applications need to consider not only technically effective treatment process, but also other key aspects of operation, maintenance and cost effectiveness. Recycling and sludge management options are needed to be addressed.

Handling of sludge is considered as a key component for selection of any treatment process. The timeframe for handling sludge depends on the design of adsorption process. Unless phosphorus is recovered from the sludge and the sludge is regenerated, the treatment utilities would have to manage this sludge. The necessity of sludge

management would not be that frequent for adsorption process. The presence of phosphorus would provide the sludge an edge for agricultural land use. Chapter 10 of this thesis discusses some options for residual management. The coagulation process on the other hand would produce sludge regularly. So, there would be regular need for maintenance and management of the sludge produced. Coagulation process would also require oven dried alum sludge regularly to operate the system. Based on the experimental findings, the coagulation process would require large doses of alum sludge and would produce a huge amount of sludge regularly. The utilities would require managing this large amount of sludge periodically. With low phosphorus removal in coagulation process, the sludge would not have a large amount of phosphorus. Therefore, agricultural application would not be a likely choice for management of the residuals generated during coagulation process.

Cost consideration was important for selection of treatment process for small-scale applications. Though quantitative cost analysis was beyond the scope of the objective for this thesis, it was roughly estimated that processing costs of $95/Mg including $5/Mg for transportation costs to oven, $45/Mg for drying and $45/Mg for transportation costs to treatment facility were less than the current disposal costs ($115/Mg) to landfill. Other relative qualitative cost issues were summarized in Table 8-2. Without an actual cost comparison, it was not realistic to comment on relative cost advantages and disadvantages.

Table 8-2 Comparative economic considerations for adsorption and coagulation process

Adsorption	Coagulation
• Adsorption as a secondary treatment option would be more effective and therefore less costly due to prior treatment • High initial costs involved for columns in series • Low maintenance cost • Agricultural reuse options for residuals might be cost effective due to large phosphorus content	• Coagulation is more like a primary treatment process. Therefore, it would treat other contaminants, making it less effective and more costly • High initial costs due to design needs for high coagulant concentrations • High maintenance costs

8.5 Conclusions

Jar tests results were shown to be reproducible. Both raw and oven dried alum sludge was not effective in removing phosphorus from municipal wastewater compared to other conventional coagulant alum. Oven dried alum sludge was not effective in removing phosphorus from both municipal wastewater and aquaculture process water. It was not even effective in removing particulate phosphorus from wastewater. There was also a large amount of sludge generated during the process, as evidenced from the total suspended solids in the sludge. The experiments conducted on different pH of 3, 5 and 7 showed that the manipulation of pH would not be effective in improving the phosphorus removal efficiencies.

Adsorption was showed to be a more effective treatment process for removing orthophosphate than coagulation. The adsorption process would be easy to operate and maintain. For the adsorption process sludge would have to be replaced once in several months or a year depending on the design of adsorption process.

9.0 SURFACE CHARACTERIZATION OF ALUM RESIDUALS

9.1 Introduction

Adsorption is known to be a surface phenomenon, as a result the surface characteristics are indicative of the nature and effectiveness of adsorption processes. The objective of this chapter was to characterize the surface of oven dried alum sludge before and after adsorption of orthophosphate. Specific surface area was measured to understand the area that may be involved in the adsorption process. Scanning electron micrographs were used to understand the surface roughness and the types of pores that may be involved. X-ray diffraction was conducted to identify the crystalline structure of oven dried alum sludge. Infrared and Ramans spectroscopy were used to evaluate the possible adsorption mechanisms involved in adsorption of orthophosphate in oven dried alum sludge.

9.2 Materials and Methods

Specific surface area of oven dried alum sludge with the grain size distribution as mentioned earlier was measured using the procedure described in Chapter 4. Six samples were done on both oven and air dried alum sludge to get average values for specific surface area. Scanning electron microscopy was done on air dried alum sludge and oven dried alum sludge before and after phosphorus (2.5 mg/L) adsorption from deionized water to understand the changes in surface roughness. X-Ray powder diffraction patterns of oven dried alum sludge were obtained from gently pressed specimens of random particle orientation with particle sizes below 0.45 μm. Infrared spectrograms and surface enhanced raman spectroscopy of alum, KH_2PO_4, oven dried alum sludge before and after phosphorus adsorption were obtained using the procedure described in Chapter 4.

9.3 Results and Discussions

9.3.1 Specific surface area

The experimental results showed that oven dried alum sludge had an average specific surface area of 3208 m^2/g with a standard deviation of 620 m^2/g. The specific surface area can be considered as high compared to a specific surface area of 900-1100 m^2/g for conventional adsorbent granular activated carbon (Cooney, 1998). Experiments conducted on air dried alum sludge found 123 m^2/g with a standard deviation of 45 m^2/g. However, another study conducted on air dried alum sludge observed a maximum specific surface area of 100 m^2/g (Makris et al., 2005a). The large specific surface area might be associated with the micro pore in oven dried alum sludge. This was probably due to the result of fast drying rate of the oven dried alum sludge. During the evaporation of water particles from the alum sludge these micro pores were probably created.

9.3.2 Scanning electron microscopy

Scanning electron micrographs on small magnification (200 x) indicated a smooth surface area on oven dried alum sludge (Figure 9-1a). However, increasing magnification (4000x and 8000x) showed the evidence of micro porous structure in oven dried alum sludge (Figure 9-1b, 9-1c). Previous study on air dried alum sludge observed sand size aggregates at similar magnifications (Kim et al. 2003a). It supported the idea of having large specific surface area for oven dried alum sludge, as micro porous structures could lead to large internal surfaces. Scanning electron micrographs at 200x and 4000x showed similar structural pattern in air dried alum sludge (Figure 9-2). The surface roughness at 4000x air dried alum sludge appeared to be smoother than oven dried alum sludge.

a) magnification = 200

b) magnification = 4000
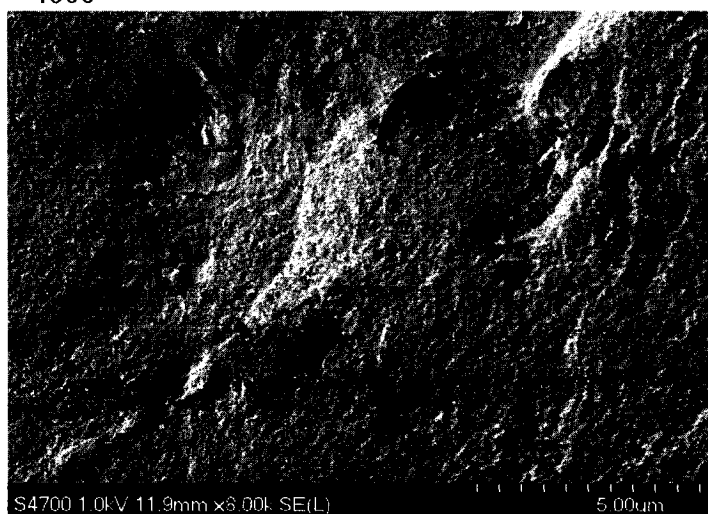
c) magnification = 8000
Figure 9-1. Scanning electron micrograph for oven dried sludge
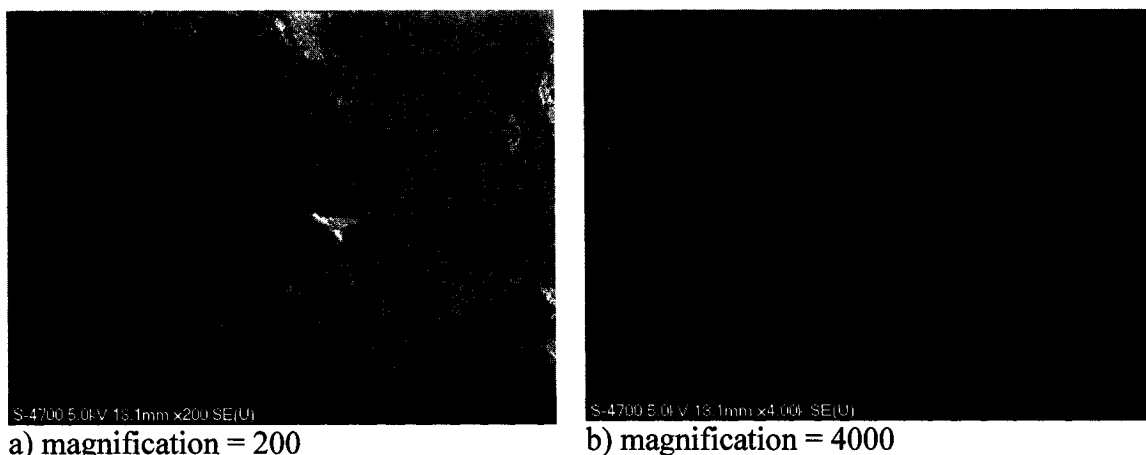
a) magnification = 200   b) magnification = 4000

Figure 9-2. Scanning electron micrograph for air dried alum sludge

The adsorption of orthophosphates on oven dried alum sludge did not affect the surface

structures much. With a magnification of 4700 times, oven dried alum sludge showed

some patches of the surfaces compared to smooth surfaces before (Figures 9-1b, 9-3a).

These patches might have been created due to adsorption of orthophosphates on the

surfaces. However, higher magnification (10000 x) did not indicate much changes in the

surface roughness (Figures 9-1c, 9-3b).
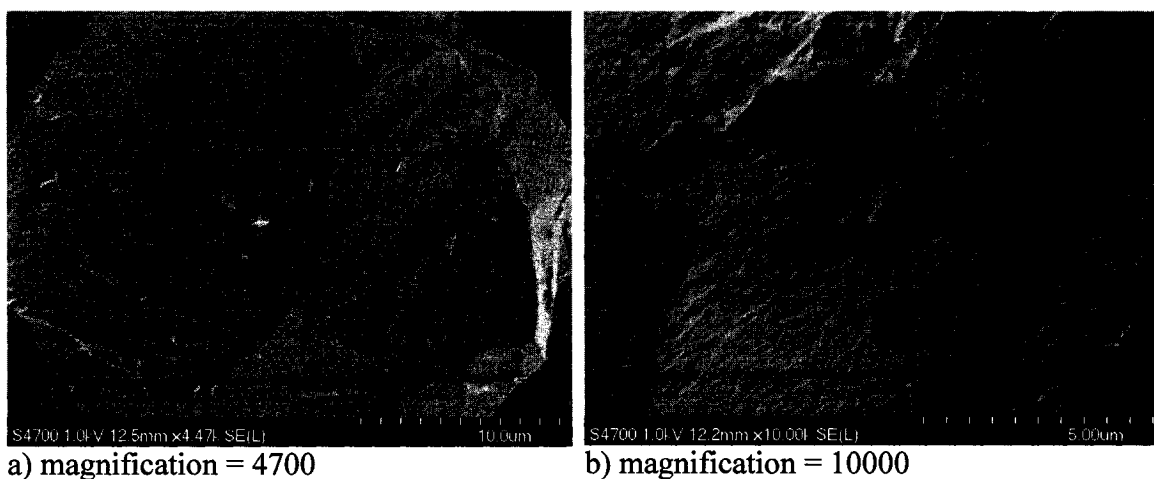
a) magnification = 4700   b) magnification = 10000

Figure 9-3. Scanning electron micrograph for oven dried alum sludge after adsorption of
phosphate

9.3.3 X-ray diffraction

Experimental results from X-ray diffraction did not show any characteristic peak in the count with the changes in incident angle of x-ray on oven dried alum sludge (Figure 9-4). The x-ray diffraction also did not change after adsorption of orthophosphate on oven dried alum sludge (Figure 9-5). It indicated that the oven dried alum sludge was amorphous in nature. Oven dried alum sludge was a by product generated from alum and raw water from Lake Major. As Lake Major did not have crystalline minerals in their water, the alum sludge from the water did not also contain crystalline minerals. Previous study conducted on air dried alum sludge in South Korea observed the presence of Kaolinite, Mica and Quartz, that was probably from raw water quality (Kim et al., 2003a). However, another study observed the amorphous nature of air dried alum sludge (Makris et al., 2005a)
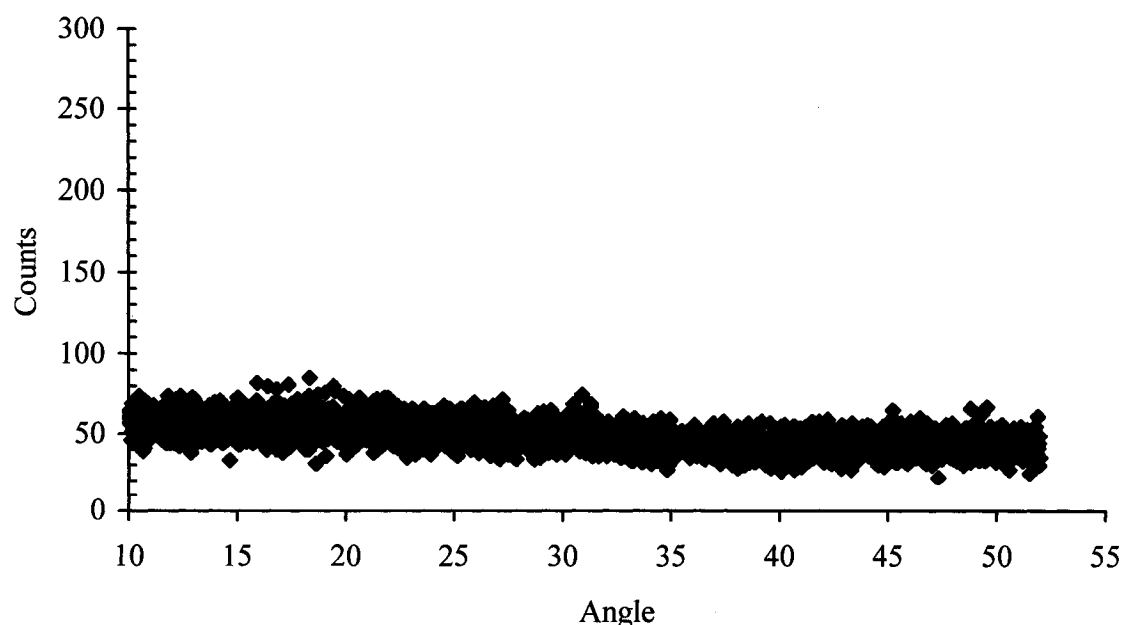
Figure 9-4. X-ray diffraction result for oven dried alum sludge
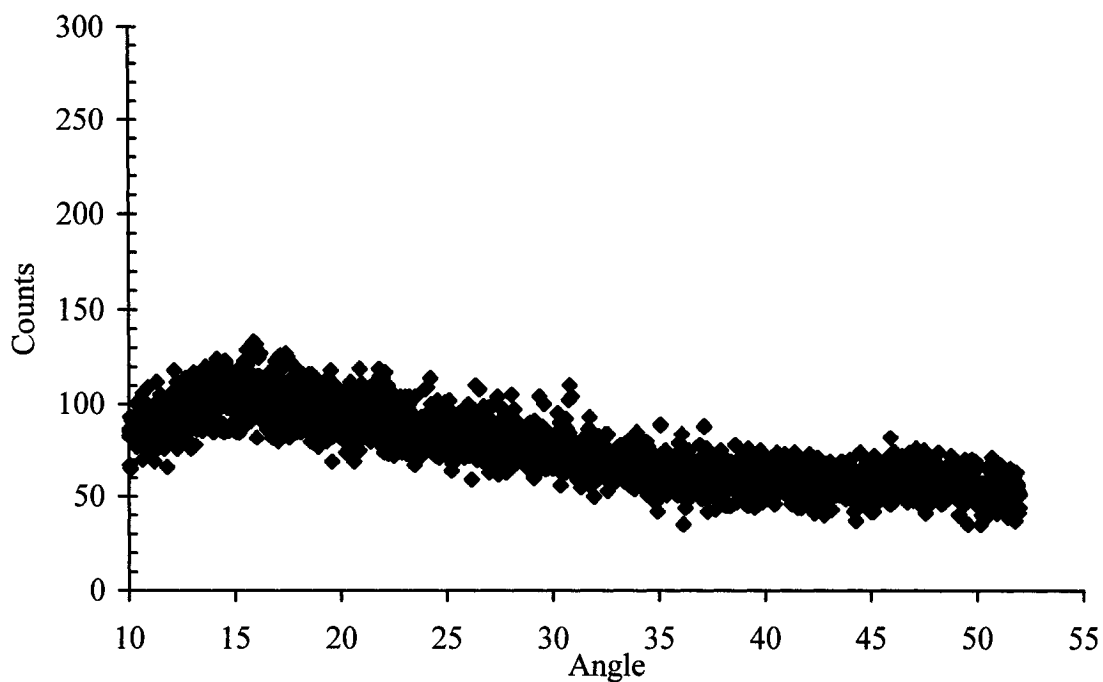
Figure 9-5. X-ray diffraction result for alum sludge after adsorption of phosphate

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9.3.4 Infrared spectroscopy

Absorbance intensity generated from infrared spectroscopy showed similar peaks for all the samples in both alum and oven dried alum sludge (Figure 9-6). Peaks at an infrared wavelength of 800 cm^{-1} indicated that the presence of sulfate ions. The literature also showed peaks for similar wavelengths for sulfate ions (Lefevere, 2004).
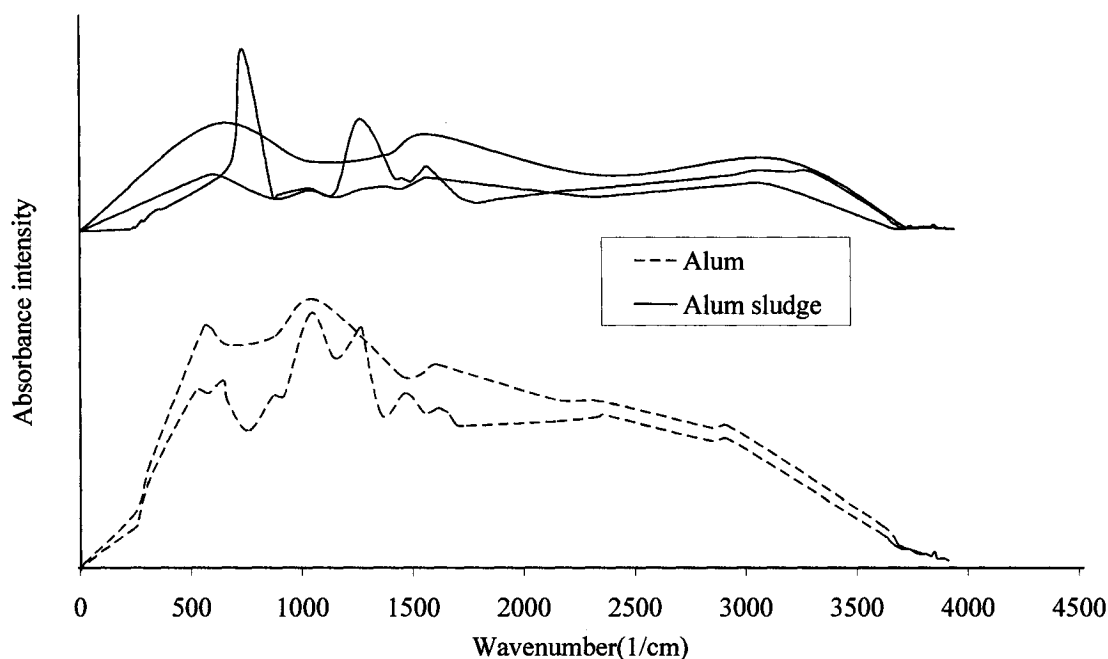
Figure 9-6. IR spectroscopic result for alum and oven dried alum sludge

Orthophosphate ions had background peaks around 850, 875, 890, 940, 990, 1075 and

1155 cm^{-1}. Typical inorganic hydroxide ions (OH$^-$) have peaks in the wavelength of

2500-4000 cm^{-1} (Al-Abadleh and Grassian, 2003). The adsorption of orthophosphate on

oven dried alum sludge decreased relative absorbance intensity caused by hydroxide ions

(OH$^-$) present in alum sludge before and after adsorption of orthophosphate (Figure 9-7).

There was also a relative increase in the absorbance intensity at wavelengths that were

characteristic for orthophosphates. It indicated the possibility of hydroxide ions being

replaced by phosphate ions. Some of the experimental results in fixed bed column tests

also indicated the possibility of leaching OH$^-$ ions after phosphorus adsorption. This idea

was supported by previous phosphate adsorption studies conducted on activated red mud,

clay minerals and manganese noodles (Pradhan et al., 1998; Parida and Mohanty, 1998;

Ioannou and Dimirkou, 1997). The possible chemical reaction that might be involved in the chemical adsorption of orthophosphate on oven dried alum sludge was:

$$3R\text{-}OH + PO_4^{3-} = 3R\text{-}PO_4 + 3OH^- \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 9\text{-}1$$
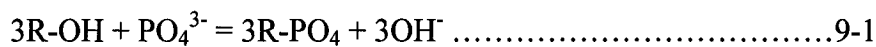
Where,

R can be aluminum based active group in the surface of alum sludge
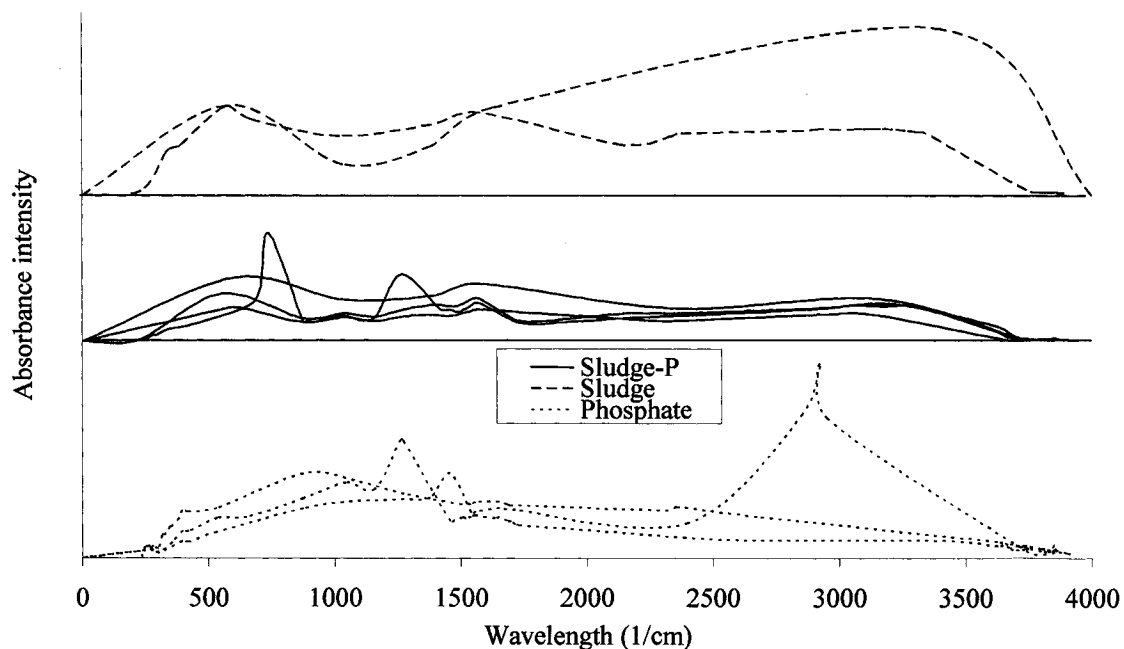
Figure 9-7. IR spectroscopic result for phosphate and alum sludge with and without phosphate

9.3.5 Ramans spectroscopy

Experimental results from raman spectroscopy showed higher raman intensity for both alum and oven dried alum sludge in the range of 0-2000 cm^{-1} wavelength (Figure 9-8). Though there were no identifiable peaks in alum sludge, there was high raman intensity in the same range as in alum. However, this range of wavelength is generally attributed to

inorganic ions. As alum sludge was a mixture of different types of ions present in the

water, there were interferences from different inorganic ions in that range of wavelength.

This was probably the reason for not observing the peak as it was found from IR

spectroscopy.
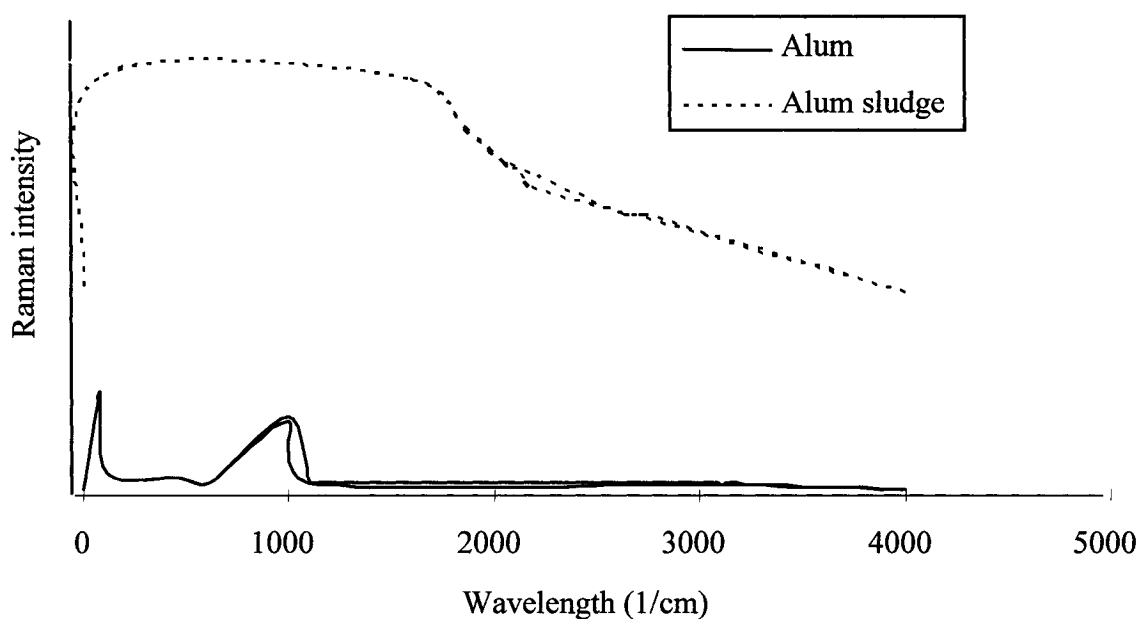
Figure 9-8. Raman spectroscopic result for alum and oven dried alum sludge

Background peak raman intensity for orthophosphate was similar to IR spectroscopy. The

adsorption of orthophosphate on oven dried alum sludge increased the relative raman

intensity around wavelengths characteristic for orthophosphate. However, a decrease in

the relative raman intensity for wavelengths that had peaks due to the presence of

hydroxide ions (OH⁻) was not clear (Figure 9-9). However, the differences in raman

intensity could not be measured quantitatively with available experimental techniques.
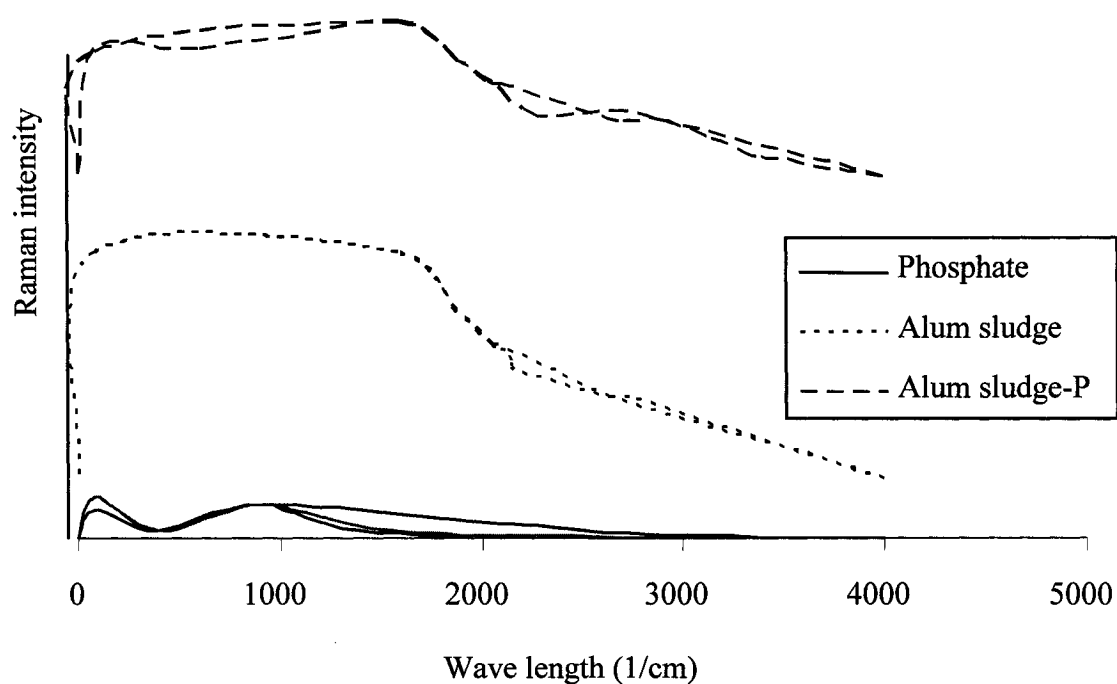
Figure 9-9. Raman spectroscopic result for phosphate and alum sludge with and without phosphate

9.4 Conclusions

Oven dried alum sludge was shown to have micro pores in their structure. From an indication of high specific surface area, oven dried alum sludge was shown to be a probable good adsorbent. X-ray diffraction experimental results showed that oven dried alum sludge was amorphous in nature. Infrared spectroscopic results indicated about the possible chemical adsorption mechanisms involved in adsorption of orthophosphate on oven dried alum sludge. It indicated the possibility of hydroxide ions being replaced by phosphate ions.

10.0 STABILITY AND RESIDUALS MANAGEMENT OF SPENT ALUM RESIDUALS

Phosphorus adsorption onto oven dried alum sludge shown in the previous chapters provided an environment friendly management option for water treatment residuals. However, the residuals generated during the process of adsorption on oven dried alum sludge are also needed to be managed. Leaching capability for surface water and land disposal methods need to be addressed.

The objective of this chapter was to determine the lachability of residuals generated from adsorption of phosphorus from small-scale wastewater on alum sludge. This chapter examined the leachate concentrations as obtained from Toxicity Characteristics Leaching Procedures (TCLP) tests as part of land based disposal options. The leaching behaviour was also compared with other types of alum sludge. This chapter also examines the leaching of aluminum from the same residuals disposed in surface water and conducted ecological risk assessment in the process.

10.1 Leachability of Sludge in Land Based Residual Disposal

10.1.1 Introduction

Water treatment plant (WTP) residuals contain varying amounts of heavy metals, nutrients and pathogens. However, it is generally not considered as hazardous waste. Disposal of alum-based WTP sludge is a recognized concern in various parts of the world (Gutierrez et al., 1998; Committee Report, 1972), mainly because of its potential to leach aluminum due to the presence of large amount of aluminum in these residuals (Tyagi et

al., 1990; Roy and Couillard, 1998). Many current WTP residuals management practices

such as lagooning, landfilling and land spreading (Lucas et al., 1991; Jonasson, 1996;

Wang et al., 1998) were developed in response to the concern associated with

conventional disposal in surface water. Alum sludge after adsorption of phosphorus goes

through physicochemical changes as discussed in Chapter 9. These changes can have

effect on the leachability of alum sludge.

10.1.2 Experimental setup

Oven dried alum sludge was used for this test. Raw, air dried and freeze thaw dried alum

sludge was also used to compare the leaching behavior of oven dried alum sludge. The

residuals generated after fixed bed column treatment of small-scale wastewater were also

used for this test to understand the effect of phosphorus treatment on the leachability of

aluminum and manganese. The calculation of leachate concentrations in residuals

generated from treatment of small-scale wastewater were conducted after considering the

aluminum and manganese leached during the fixed bed column tests in Chapter 7.

10.1.3 Results and discussions

10.1.3.1 Leaching Behavior of Alum Sludge

TCLP tests conducted on different types of alum sludge showed that dried alum sludge

had lower tendency to leach aluminum and manganese than raw alum sludge (Figure 10-

1). Aluminum leaching was decreased 59%, 79% and 76% after oven, air and freeze thaw

dried respectively. Reduction in manganese leaching after similar drying was 69%, 36%

and 48% for oven and air and freeze thaw dried alum sludge. Probably, it was because of

the structural variation in alum sludge surfaces during drying process. Air drying was not

effective in reducing manganese leaching. However, both of the drying processes were

effective in reducing aluminum leaching. There were no specific guideline concentrations

for aluminum and manganese. Modeling is normally done for individual ecosystems on

what concentrations of aluminum and manganese can be allowed for land based polluters.
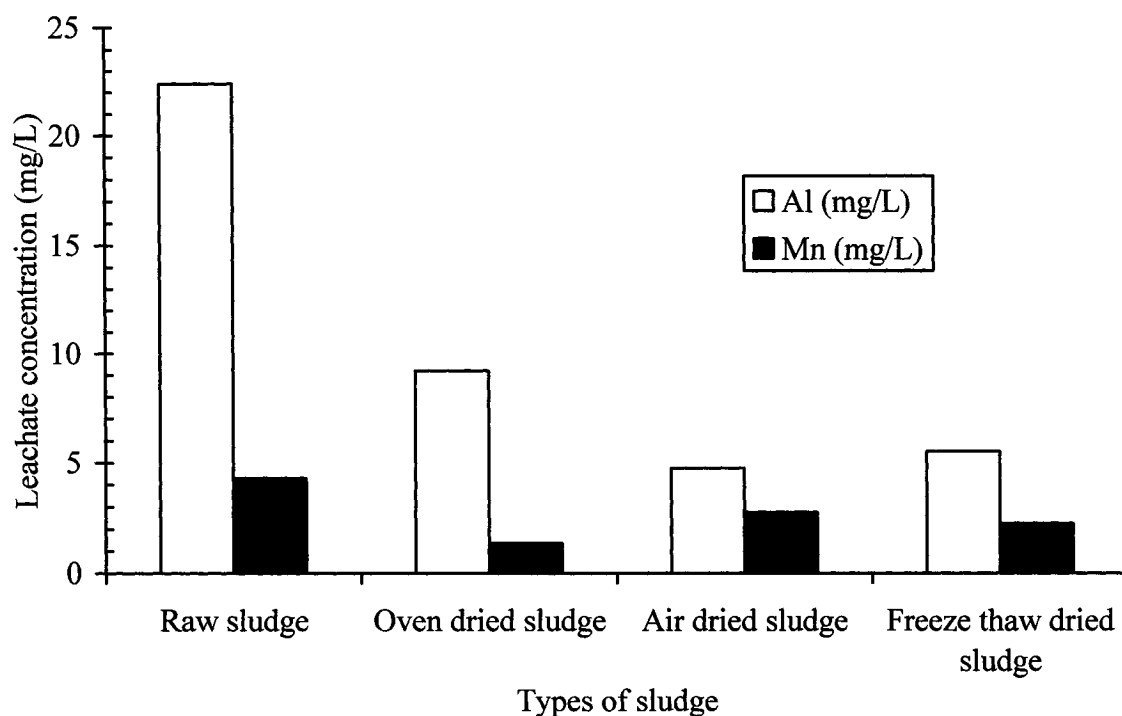
Figure 10-1. TCLP leaching results conducted on different types of alum sludge

10.1.3.2 The Effect of Phosphorus Treatment on Leachability

TCLP tests conducted on phosphorus treated oven dried alum sludge showed that

phosphorus treatment was mostly effective in reducing aluminum leaching (Figure 10-2).

It reduced aluminum in 54%, 63% and 97% for municipal wastewater, aquaculture

process water and biofilter wastewater respectively. When treated with aquaculture water

and biofilter wastewater, leaching of manganese decreased 75% and 78% respectively. However, municipal wastewater increased the manganese leaching behaviour of oven dried alum sludge up to 98%. Phosphorus adsorbed on oven dried alum sludge did not leach considerably. Phosphorus concentration in the leachate was less than 0.5 mg/L for various residuals. It indicated that phosphorus was most likely bound with aluminum and manganese. Previous study revealed the formation of stable compound after phosphorus adsorption of aluminum hydroxide (Makris et al., 2005b). However, high phosphorus and manganese leaching for residuals generated after treatment of secondary municipal wastewater indicated that the phosphorus was not strongly bonded with manganese.
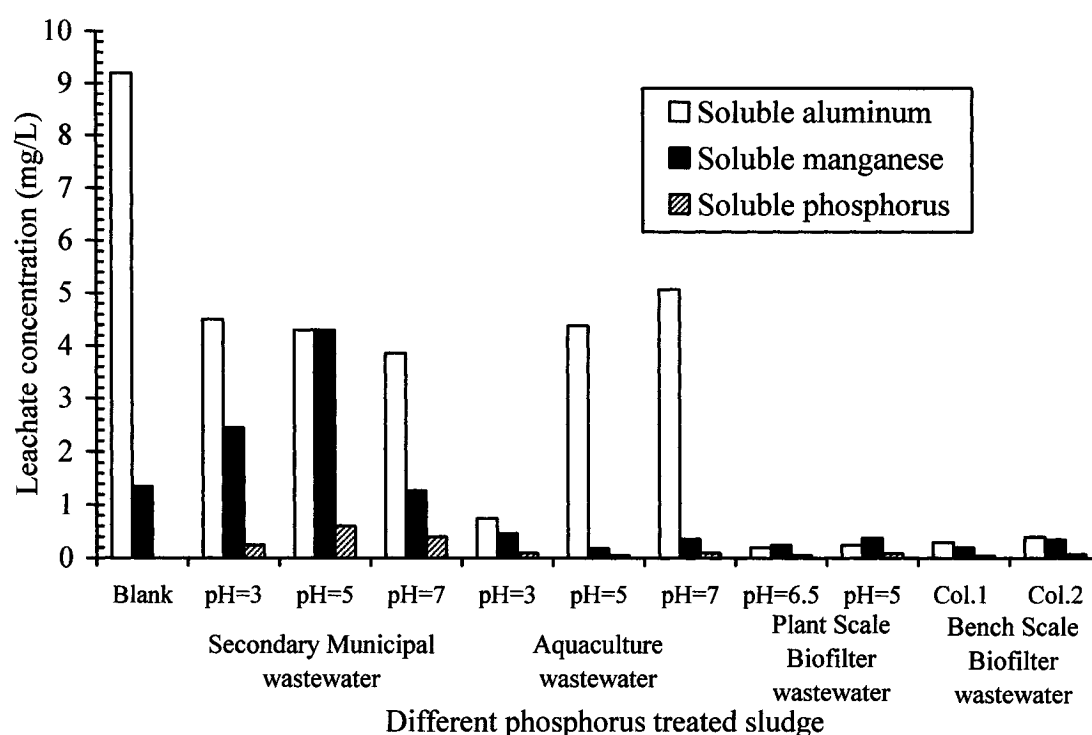
Figure 10-2. Effect of phosphorus treatment in leaching of contaminants

10.2 Risk Assessment of Surface Water Disposal

10.2.1 Introduction

Alum sludge disposal in surface water was known to cause aluminum toxicity in aquatic organisms (Abdullah et al., 1995; George et al., 1991). The increasing occurrences of acid precipitation created low pH in the surface waters, liberating aluminum ions from solid phase to aquatic phase (Hutcheson and Odense, 1984; Holtze and Hutchinson, 1989). There are large amounts of alum sludge generated in water treatment plants, many of which dispose alum sludge directly into surface waters (Cornwell et al., 2000).

The objective of this study was to conduct an ecological risk assessment from residual disposal into the surface water on fish. Aluminum being the major component in alum sludge was considered for assessment of toxicity. The leaching of phosphorus that was adsorbed onto oven dried alum sludge was also assessed. Experiments conducted to obtain expected environmental concentration (EEC) of aluminum and phosphorus leaching on waters from Pockwock Lake, Nova Scotia. The sludge generated from fixed bed column tests of small-scale wastewater (Chapter 7) was also used on water from Pockwock Lake. However, aluminum speciation was not conducted as part of these experiments. The EEC of aluminum estimated from these experiments was further used to calculate risk on aquatic species.

10.2.2 Experimental setup

Surface water leaching experiments were conducted on oven dried alum sludge for estimation of EEC. Lake water without addition of any sludge was considered as a blank.

Water from Pockwock Lake was hypothetically chosen for this test. Oven dried alum sludge was tested at three pH levels of 4, 5.5 and 7. Raw, air dried and freeze thaw dried alum sludge were also used to compare the leaching behaviour of oven dried alum sludge. The residuals generated after fixed bed column treatment of small-scale wastewater were also used for this test to understand the effect of phosphorus treatment on the leachability of aluminum. The calculation of leachate concentrations in residuals generated for treatment of small-scale wastewater were conducted after considering the aluminum leached during the fixed bed column tests in Chapter 7.

10.2.3 Problem formulation

Ecological risk assessment was conducted based on USEPA guideline (Landis and Yu, 1999). The framework for this project is summarized in Figure 10-3. It showed different components of ecological risk assessment and their relevance to water treatment management. The sharing of information in the flow chart is discussed in this Chapter sequentially. There are both natural and anthropogenic reasons for increasing aluminum concentrations in the environment (Kemp et al., 1978; Drndarski, 1979). Alum sludge disposal is one of the major sources of aluminum in the environment (Abdullah et al., 1995; Yannai et al., 1978; Rubin and Blocksidge, 1979). About 11 % of the total residuals generated in surveyed water treatment plants each year in United States were disposed to surface water (Cornwell et al., 2000). It indicated the extent of problems involved with the disposal of alum sludge in surface water.
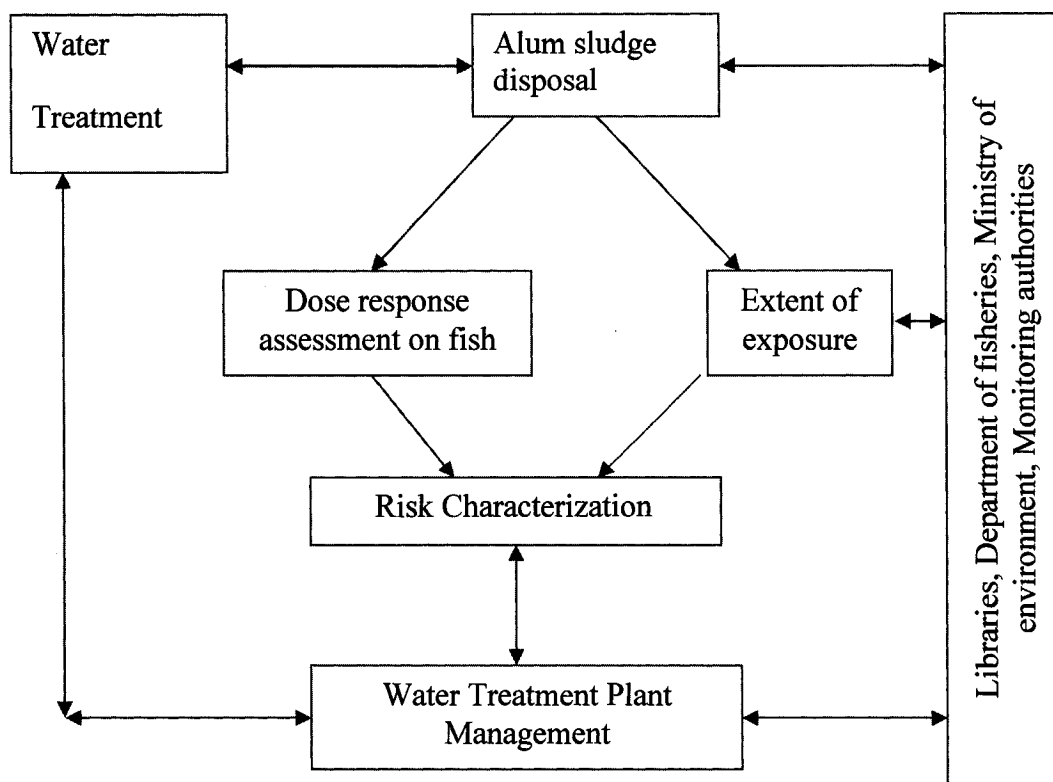
Figure 10-3. Schematic of framework for ecological risk assessment

10.2.4 Aluminum chemistry and speciation in water

The chemical speciation of aluminum in natural water regulates its mobility,

bioavailability and toxicity. Aluminum normally undergoes hydration reaction in aqueous

systems to an extent governed by the ligand properties and concentrations of aluminum,

and hydrogen ion (Faust and Aly, 1999). Hydrolysis increases as the solution pH

increases, resulting in a series of aluminum hydroxide complexes. Alum sludge is mostly

composed of these series of aluminum hydroxide complexes. The soluble species at alum

sludge are higher in pH below 6 (Figure 10-4). Speciation in a certain surface water

system changes with seasonal variation and other anthropogenic reasons. Free and

monomeric aluminum has been found to have the highest toxicity among all the species

available in water. Organic aluminum produces the least toxicity among the available

aluminum species. Relative aluminum speciation can change with changing pH in water.

Tests conducted on alum sludge extracts in Calgary showed around 50% filtered total

aluminum (George et al., 1991). Acidification increases the amount and availability of

aluminum to aquatic organism (Stokes and Hutchinson, 1976; Schindler et al., 1980;

Gardner et al,. 2002). The increase in aluminum level may be the result of its replacement

by hydrogen ion through cation exchange with the sediment (Hall et al., 1980; Malmer

1976) or the solubility changes with metal ions (Cronan et al., 1978).
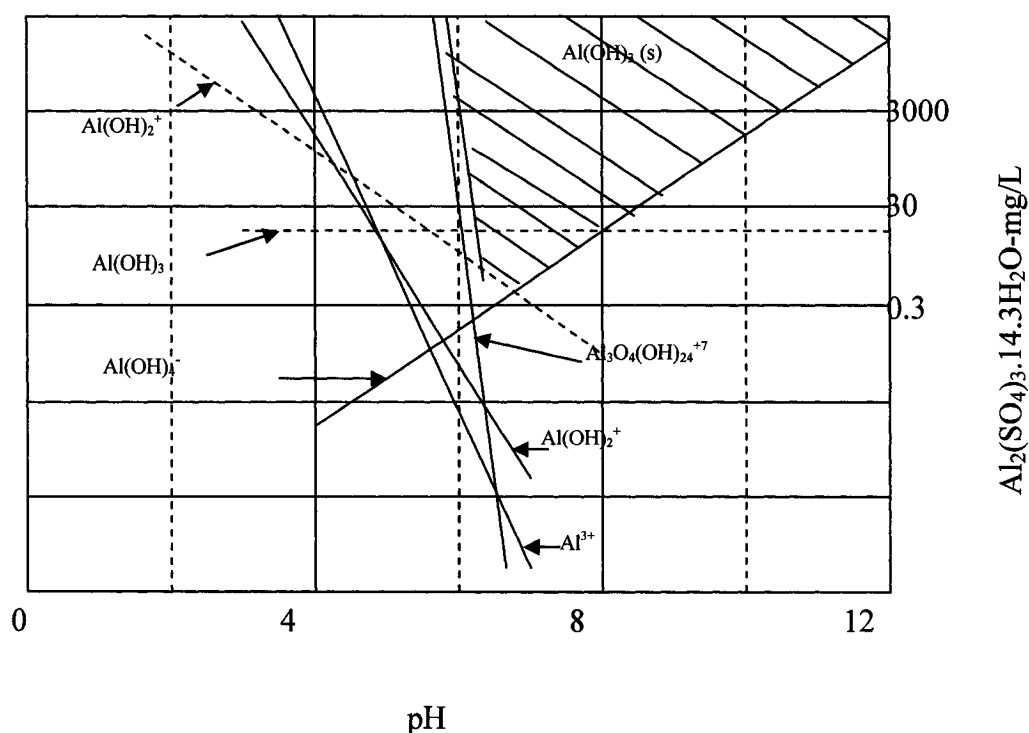
Figure 10-4. Various aluminum species at different pH levels (adapted from Faust and
Aly, 1999)

10.2.5 Interaction with aquatic habitat

Aluminum in low concentration is not very harmful to aquatic habitat. However at low

pH levels, aluminum can be deadly for aquatic habitat (Havas, 1986). Aluminum can be

toxic to both flora and fauna. Toxicity is dependent on species of aquatic habitat, also being affected by different life stages of fish. Avoidance of aluminum was observed on Rainbow Trout (Exley, 2000). Results have shown that aluminum in concentration within 6-12 mg/L can be a micronutrient for some algal species (Havas, 1986). Aluminum appeared to have mixed effect on microcrustaceans (Havas, 1986). Aluminum has been found to inhibit active uptake of Ca^{2+} by Crayfish during postmolt (Havas, 1986). Insects were not affected by aluminum. Some species of Rotifiers appear to be particularly aluminum and acid tolerant (Havas, 1986). For fungus, alum addition to a nutrient solution completely inhibited germination at pH 4.8, but had little effect at pH 7.0. Bacteria have shown to be tolerant to aluminum concentration within 100 mg/L.

Alum sludge disposal in the surface water has been considered toxic, as it increases aluminum concentration in the water. However, researches were very limited for alum sludge related toxicity. Ramamoorthy (1988) worked on a laboratory simulation of an aquatic system to show that lower pH levels associated with alum sludge disposal could be toxic. It also revealed that lower pH is not very toxic, when applied to water with lower turbidity. Algal growth inhibition was observed in alum sludge extracts obtained at pH 5 (George et al., 1995). The mortality for Fathead Minnow was also not found significant (<20%).

10.2.6 Evaluation of effects

Acute toxicity of aluminum was observed in several aquatic species (Tandjung, 1982; Baker, 1981; Havens, 1990; Havens, 1993; Soucek et al., 2001; Chu and Chow, 2002).

Acute toxicity can be both lethal and sub lethal in nature. George et al. (1991) conducted

Microtox Toxicity Test, Protozoan Toxicity Test and algal assay on alum sludge extracts

from ten different water treatment utilities across United States and Canada. Microtox

Toxicity test did not demonstrate acute toxicity. No inhibition occurred during Protozoan

Toxicity Test. The algal bioassay using *Selenastrum capricornutum* showed the greatest

response for exposure to alum extracts.

Aluminum in water has proven to produce chronic toxicity (Allin and Wilson, 1999;

Baker, 1981; Cleveland et al., 1986; France and Stokes, 1987; Biesinger and Christensen,

1972; Burton and Allen, 1986). Sub lethal effects of reduction in appetite, metabolism

and behavior have been also documented (Petrich and Reish, 1979; Wilson et al., 1994;

Allin and Wilson, 1999). However, chronic toxicity tests from alum sludge extracts on

Ceridaphnia and Fathead Minnow did not show significant mortality (George et al.,

1991).

10.2.7 Dose response assessment

The selection of an appropriate endpoint is difficult. Assessment endpoints in this case

are inferred by the use of measurement endpoint. The measurement endpoint is selected

as the percent mortality of fish in case of acute lethal toxicity. The mortality of fish is

associated with certain concentration of aluminum under a certain pH in several exposure

periods. Changes in regular behavior of aquatic species are chosen as endpoint for

sublethal toxicity.

The toxicity of aluminum as presented by dose response assessment was tested based on

a range of aluminum concentration and response to fish (Baker, 1981; Tandjung, 1982).

These assessments were based on various species of fish tested. LC_{50} values were low for

most of the species (Table 10-1). However Fathead Minnow showed higher resistance

compared to other species. Mummichog and Mosquito fish have showed the lowest

resistance based on the lowest LC_{50} values. Dose response assessment conducted on

Brook Trout by Tandjung (1982), were taken for the assessment of risk in this thesis

(Table 10-2). Higher hardness values have higher LC_{50} values compared to lower

hardness. As lower hardness values produced the most critical condition for Brook Trout,

the tests conducted on a hardness value of 2 mg/L was chosen for calculation of risk. This

hardness values are also close to the hardness value for Pockwock lake water (5.1 mg/L)

(Halifax Regional Water Commission, 2004). Based on the tests conducted by Tandjung

(1982), No Observed Effects Concentrations (NOEC) of 0.1 mg/L was selected for

aluminum toxicity for acute toxicity (Table 10-2). Chronic toxicity was not documented

with a rigorous dose response assessment. Cardwell et al. (1993) found 87 μg/L of NOEC

for chronic lethal toxicity. Chronic sub-lethal effects were evident at an aluminum

concentration of 30 μg/L for Rainbow Trout at a pH of 5.2 (Allin and Wilson, 1999).

Dose response assessments were conducted in laboratory setup with aluminum and pH

were the only toxicants. However, in natural river systems, there would be other toxicants

present in the river. Therefore, the resistance showed by fish under laboratory condition

would not be expected in the river system.

Table 10-1. Toxicity of aluminum to fish (adapted from Habs et al., 1997).

Organism	Hardness (mg/L)	pH	96-hr LC$_{50}$ (mg/L)	Reference
Atlantic Salmon	5	4.90-5.06	0.075-0.463m	Rosseland and Skogheim, 1984; Skogheim and Rosseland, 1986)
Brown Trout	5	4.80-4.94	0.313-0.463m	Skogheim and Rosseland, 1986
Mummichog	6.6-18.8		3.6-31.5n	Dorfman, 1977
Mosquito fish		4.3-7.7	133-235n	Wallen et al., 1957
Fathead Minnow	38	7.4	3.3-5.6	Mayer and Ellerseick, 1986
American flag fish	6.0	5.8	0.095	Hutchinson and Sprague, 1986

Table 10-2. Response of Brook Trout under various doses of aluminum (pH = 5.6).

Hardness = 40 mg/L			Hardness = 18 mg/L			Hardness = 2 mg/L		
Al (mg/L)	96-hr mortality (%)	LC$_{50}$ (mg/L)	Al (mg/L)	96-hr mortality (%)	LC$_{50}$ (mg/L)	Al (mg/L)	96-hr mortality (%)	LC$_{50}$ (mg/L)
0.0	0		0	0		0	0	
2.0	0		2	30		0.1	0	
3.5	0-10	6.2-7.0	3	40-60	2.8-4	0.2	0-10	0.36-0.39
5.0	20-40		4	50-70		0.3	0-20	
7.5	30-50		5	60-80		0.4	40-70	
10.0	40-70		8	70-90		0.5	90-100	
16.0	100		13	100		1.0	100	

10.2.8 Exposure assessment

Aluminum is exposed from alum sludge through direct disposal to surface water.

Aluminum in the environment is mostly partitioned within water and sediment.

Aluminum in alum sludge is soluble in water and dilute acid and insoluble in alcohol.

Generally, aluminum in other forms slowly precipitates to aluminum hydroxide.

Environmental restoration division (1999) provided a Bio-concentration Factor (BCF)

from water to fish as 10. Cleveland et al. (1991) found a BCF of 215. The variability in

BCF values was due to variability in species.

Aluminum is found in aquatic species in a range of concentrations. Aluminum is taken up

by fish through gills. Cleveland et al. (1986) exposed Brook Trout eggs, larvae and

juveniles to 0.3 mg/L aluminum at various pH levels. After an exposure period of 30

days, aluminum levels were 112-398 mg/kg for larvae and juveniles at pH 5.28. The

corresponding aluminum levels at a pH 7.24 were 12-33 mg/kg, and at pH 4.44 were 17-

71 mg/kg. Several other studies showed mixed aluminum uptake by several fish species

(Cleveland et al., 1991; Skogheim et al., 1984; Wicklung Glynn et al.; 1992).

10.2.9 Risk characterization

The risk posed by alum sludge is a combination of both qualitative and quantitative

aspects of risk. Qualitative risk was discussed earlier. Estimation of risk is normally

calculated as an indicator "Risk Quotient" (RQ). RQ is normally calculated based on a

specific contaminant and receptor. The mathematical formula being used in the

calculation of RQ is:

$$RQ = \frac{EEC}{TRV} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 10\text{-}1$$

Where,

    EEC = Estimated environmental concentration, concentration found in natural
environment, can also be found from laboratory based experiments.

TRV = Toxicity reference value = NOEC (in this investigation), calculated from laboratory based experiments for toxic effects on particular species.

EEC values were obtained from the experiments conducted on Pockwock lake water. Experimental results indicated a decrease in the risk from the disposal of alum sludge on Pockwock Lake (Table 10-3). Raw and all other dried sludge reduced RQ values below 1 consistently for acute lethal and chronic lethal toxicity. However, all the different types of alum sludge were shown to produce chronic sub lethal risk to fish. The changes in pH values in oven dried alum sludge did not show considerable effect on the RQ values observed. The reduction in risk may also be associated with high aluminum concentration in Pockwock Lake.

Experimental results on the residuals generated in Chapter 7 consistently showed a decrease in RQ values (Table 10-4). The residuals generated from the treatment of aquaculture process water at pH values 5 and 7 and Bench scale biofilter water showed no risk for disposal in pockwock lake water. Residuals generated from treatment at a pH value 3 were shown to have higher risk for surface water disposal than residuals generated at other pH values. However, the disposal of these residuals appeared to have increased phosphorus concentration in most of the cases. The residuals generated from treatment of aquaculture water at a pH of 7 appeared to have decreased the phosphorus concentration. However the phosphorus concentrations were mostly below 0.01 mg/L, except from the tests conducted on residuals generated from the treatment of plant scale biofilter wastewater.

Table 10-3. Soluble concentration of aluminum from alum sludge and risk quotient for aluminum toxicity

Type of alum sludge	pH	Al (mg/L)	Toxicity test	TRV (mg/L)	RQ
Blank	6.14	0.163	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	1.63 1.87 5.43
Raw sludge	5.86	0.062	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	0.62 0.71 2.07
Air dried sludge	5.68	0.057	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	0.57 0.66 1.9
Freeze thaw dried sludge	6.53	0.064	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	0.64 0.74 2.13
Oven dried sludge	5.93	0.069	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	0.69 0.79 2.30
Oven dried sludge	4	0.075	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	0.75 0.86 2.5
Oven dried sludge	5.5	0.060	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	0.60 0.69 2
Oven dried sludge	7	0.069	Acute, lethal Chronic, lethal Chronic, sub-lethal	0.1 0.087 0.030	0.69 0.79 2.30

Table 10-4. Aluminum and phosphorus concentrations and risk quotient for aluminum toxicity

Type of wastewater	pH	Al (mg/L)	phosphorus (mg/L)	Toxicity test	TRV (mg/L)	RQ
No treatment	5.93	0.069	0.004	Acute, lethal	0.1	0.69
				Chronic, lethal	0.087	0.79
				Chronic, sub-lethal	0.030	2.30
Municipal (at pH 3)	6.56	0.054	0.008	Acute, lethal	0.1	0.54
				Chronic, lethal	0.087	0.62
				Chronic, sub-lethal	0.030	1.80
Municipal (at pH 5)	6.07	0.041	0.007	Acute, lethal	0.1	0.41
				Chronic, lethal	0.087	0.47
				Chronic, sub-lethal	0.030	1.37
Municipal (at pH 7)	6.52	0.030	0.007	Acute, lethal	0.1	0.30
				Chronic, lethal	0.087	0.35
				Chronic, sub-lethal	0.030	1.00
Aquaculture (at pH 3)	6.98	0.052	0.007	Acute, lethal	0.1	0.52
				Chronic, lethal	0.087	0.60
				Chronic, sub-lethal	0.030	1.73
Aquaculture (at pH 5)	6.09	0.024	0.006	Acute, lethal	0.1	0.24
				Chronic, lethal	0.087	0.28
				Chronic, sub-lethal	0.030	0.80
Aquaculture (at pH 7)	6.82	0.028	0.003	Acute, lethal	0.1	0.28
				Chronic, lethal	0.087	0.32
				Chronic, sub-lethal	0.030	0.93
Pilot biofilter (at pH 6.5)	6.58	0.032	0.011	Acute, lethal	0.1	0.32
				Chronic, lethal	0.087	0.37
				Chronic, sub-lethal	0.030	1.07
Pilot biofilter (at pH 5)	6.48	0.061	0.016	Acute, lethal	0.1	0.61
				Chronic, lethal	0.087	0.70
				Chronic, sub-lethal	0.030	2.03
Bench scale biofilter (column1)	6.41	0.021	0.007	Acute, lethal	0.1	0.21
				Chronic, lethal	0.087	0.24
				Chronic, sub-lethal	0.030	0.70
Bench scale biofilter (column2)	6.42	0.025	0.006	Acute, lethal	0.1	0.25
				Chronic, lethal	0.087	0.29
				Chronic, sub-lethal	0.030	0.83

10.2.10 Risk management

The risk posed by alum sludge on aquatic habitat, especially on fish, has been in the focus for the past few years. Some of the treatment plants started to look for alternative reuse

and disposal options of alum sludge. Some of the water treatment plant in Nova Scotia has shifted to landfill disposal of alum sludge (Lucas et al., 1994). However, the experimental results in this project showed that alum sludge can also reduce risk on fish, especially after adsorption of phosphorus. Therefore, case specific management decisions are needed. Even shifting of the land based alum sludge application requires a better understanding of the risk for management personnel in concern.

10.3 Conclusions

The results indicated that oven dried alum sludge were less susceptible to leaching of aluminum and manganese compared to raw alum sludge when considered for land based disposal. Oven dried alum sludge also showed comparable leachability to other dried alum sludge. Phosphorus treatment using oven dried alum sludge showed considerable reduction in aluminum leaching. However, managanese leaching was also low, with an exception of residual generated after treatment of secondary municipal wastewater. Phosphorus leaching was low indicating strongly bound with aluminum.

Aluminum toxicity generated from alum sludge disposal to surface water produced huge concerns on the fish habitat. However, within the scope of the experiments conducted, the disposal of alum sludge was shown to reduce the risk on fish. However the dried alum sludge showed lower risk imposed on fish than raw alum sludge. pH did not appear to have considerable effect on the risk of fish. Within the scope of the thesis, the adsorption of phosphorus onto oven dried alum sludge showed a marked reduction in risk for a probable disposal in surface water. There was some increase in the phosphorus

concentrations. However, phosphorus concentrations were lower than 0.01 mg/L for most of the residuals tested.

Experimental findings indicated the residuals generated during adsorption of phosphorus in oven dried alum sludge would not cause alarming level of aluminum leaching, rather it reduced aluminum leachability. Therefore, there were low chances of these residuals being a problem for disposal.

11.0 CONCLUSIONS AND RECOMMENDATIONS

This investigation used bench scale experiments to study the effectiveness of oven dried alum sludge for removal of orthophosphate from small-scale wastewater applications. Maintaining an objective of evaluating adsorption as a process option, the research takes a fundamental approach to understanding phosphorus removal in small-scale wastewater applications.

11.1 Conclusions

A) Oven dried alum sludge was effective in adsorbing orthophosphate from both deionized water and secondary municipal effluent. Oven dried alum sludge also performed comparable phosphorus removal capability to other conventional adsorbents.

B) Water quality and physical characteristics affected the performance. The effect of pH on effluent phosphorus concentration was statistically insignificant in batch adsorption tests. However the effect of pH on breakthrough pore volume in fixed bed column tests was the only instance found to be significant for 2.5 mg/L of phosphorus. High initial phosphorus concentration was found to generate higher adsorption density than low initial phosphorus concentration, although differences in phosphorus removals were not that considerable. Particle size, with a few exceptions was found to have significant effect on the final phosphorus concentrations in batch tests and breakthrough pore volumes in fixed bed column tests.

C) Oven dried alum sludge effectively removed phosphorus from small-scale wastewater applications. The phosphorus removal capability of oven dried alum sludge from small-scale wastewater was comparable and even better than phosphorus removal from deionized water. The phosphorus removal varied with the variability in wastewater characteristics. The removal of total phosphorus was not as effective as the removal of orthophosphates. The effluent pHs were mostly suitable for disposal in surface water without any pH treatment.

D) Alum sludge was not effective in removing phosphorus from wastewater as a coagulant. High alum sludge concentrations indicated large amount of sludge generation. Variation in pH was not effective in improving the phosphorus removal efficiencies. Adsorption was more effective treatment process for removing orthophosphate than coagulation. Adsorption process would have to handle sludge once in several months or a year depending on the design of adsorption process, making it easy to operate and maintain.

E) Oven dried alum sludge had micro pores in their structure. From an indication of high specific surface area, oven dried alum sludge was a good adsorbent. Infrared spectroscopic results indicated the possible replacement of hydroxide ions by orthophosphate ion during adsorption of orthophosphate on oven dried alum sludge.

F) Dried alum sludge generated in Lake Major Water Treatment Plant had a reduced leachability than raw alum sludge in a land based disposal system. The leachability in

oven dried alum sludge was also comparable to other dried alum sludge. Adsorption of phosphate on oven dried alum sludge also showed reduced aluminum leachability. With an exception of residuals generated after treatment of secondary municipal effluent, all other residuals appeared to have lower manganese leachability than oven dried alum sludge. All types of dried alum sludge were found to reduce aluminum toxicity in Pockwock Lake. This information was also translated into lower risk involved for disposal of dried alum sludge in surface water. The residuals generated after adsorption of phosphate on oven dried alum sludge consistently showed lower leachability of aluminum than oven dried alum sludge. This implied that adsorption of phosphate onto oven dried alum sludge reduced the risk imposed on aquatic species after disposal of oven dried alum sludge. However, the experimental results also found an increase in phosphorus leaching after adsorption of orthophosphate onto oven dried alum sludge.

11.2 Recommendations

Results from this investigation could be expanded in scope for future projects. Specific recommendations for future research are summarized below.

- Pilot scale studies would be a useful extension to investigate the effectiveness of oven dried alum sludge for removal of phosphate in small-scale wastewaters, which would help to predict the uncertainties that bench scale experiments could not identify. Thus it is recommended that pilot scale studies should be done prior to application of this technology as a full scale treatment option for small-scale wastewater.

- It is recommended that adsorption studies investigate behavior of orthophosphate on alum sludge with other competing ions in wastewater. There might be several

different types of ions to compete for adsorption sites. However, target wastewaters characteristics are needed to be investigated for relevant competing ions in wastewater.

- It is recommended that mathematical modeling be done using both deterministic and probabilistic approach. However, alum sludge is not a homogenous material. Therefore, deterministic theories might not be suitable for explaining adsorption of orthophosphate on oven dried alum sludge. Probabilistic approach, including artificial neural network can be a valuable tool for mathematical explanation of orthophosphate adsorption on oven dried alum sludge.

- It is recommended that surface characterization be done extensively in future for better understanding of the surface behavior of oven dried alum sludge. Alum sludge is a new adsorbent. Therefore, there are so many surface characteristics that are unexplored. Recent and emerging technologies in surface chemistry can bring useful new theories to address orthophosphate adsorption on oven dried alum sludge.

- It is recommended that extensive leachability studies can be conducted for better residual management decisions for the operators of small-scale wastewater utilities. Both land based and surface water based disposal options can be explored. These studies can also explore land based agricultural reuse options as there are high nutrient values in these residual. This study would support the idea of sustainable technological solution.

12.0 REFERENCES

Abdullah, M.P., Baba, I., Sarmani, S., and Erdawati 1995. Distribution of aluminum from alum sludge in water and sediment. *Marine freshwater research*, 46:159-165.

Aguilar, M.I., Saez, J., Llorens, M., Soler, A., and Ortuno, J.F. 2002. Nutrient removal and sludge production in the coagulation-flocculation process, *Water Research* 36: 2910-2919.

Al-Abadleh, H.A., and Grassian, V.H. 2003. FT-IR Study of Water Adsorption on Aluminum Oxide Surfaces. *Langmuir* 19:341-347.

Allin, C. J., and Wilson, R. W. 1999. Behavioral and metabolic effects of chronic exposure to sublethal aluminum in acidic soft water in juvenile rainbow trout (Oncorhynchus mykiss). *Canadian Journal of Fisheries & Aquatic Science*, 56:670-678.

Andersson, C., Tendaj, M., and Rothman, M. 1992. Filtration at Bromma sewage treatment plant. *Water Science and Technology* 25(4-5):59-66.

APHA-AWWA-WEF 1995. *Standard Methods for the Examination of Water and Wastewater*, 19th ed. APHA, AWWA and WEF, Washington D.C.

ASTM (American Standards Testing Materials) 2000. Determination of adsorptive capacity of activated carbon by aqueous phase isotherm technique. D 6586-00, 15(1).

Ayaz, S.C., and Saygin, O. 1996. Hydroponic tertiary treatment. *Water Research* 30(5):1295-1298.

Baghdadi, Z.A., Fatani, M.N. and Sabban, N.A. 1995. Soil modification by cement kiln dust. *Journal of Materials in Civil Engineering* 7 (4), 218-222.

Bagyinszki, E.F.G., and Vimola, D. 2000. EU legislation concerning wastewater treatment – tasks for wastewater treatment developments in Hungary. *Water Science and Technology*, 41(9):1-5

Baker, J. P. 1981. *Aluminum toxicity to fish as related to acid precipitation and adirondack surface water quality*. PhD thesis submitted to Cornell University, USA.

Baldwin, W.W., Monteith, H.D. and Warriner, T.R. 1974. *Phosphate removal using waste alum sludge from water purification*. Civil engineering research report CE74-1, submitted to the Department of Civil Engineering, Royal Military College of Canada, Kingston, ON.

Barnard, J.L. 1975. Biological Nutrient Removal without addition of Chemicals. *Water Research* 9(5-6):485-490

Biesinger, K. E., and Christensen, G. M. 1972. Effects of various metals on survival, growth, reproduction, and metabolism of Daphnia magna. *Journal of Fisheries Research Board of Canada* 29:1691-1700.

Boller, M., and Deplazes, G. 1990. Small wastewater treatment plants in Switzerland. *Water Science and Technology* 22(3-4):1-8.

Bubba, M.D., Arias, C.A., and Brix, H. 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Water Research* 37(14):3390-3400.

Buer, D. T. R. 2003. *Enhancement of Activated Sludge Plants by Lamellas in Aeration Tanks and Secondary Clarifiers* [online]. www.isa.rwth-aachen.de/docs/e21560a.pdf [2003, 22 March]

Burton, T. M., and Allan, J. W. 1986. Influence of pH, aluminum, and organic matter on stream invertebrates. *Canadian Journal of Fisheries and Aquatic Science* 43:1285-1289.

Cameron, K, Madamootoo, C., Crolla, A., and Kinslay, C. 2003. Pollutant removal from municipal sewage lagoon effluents with a free-surface wetland. *Water Research*, 37:2803-2812.

Cardwell, R. D., Parkhurst, B. R., Warren-Hicks, W., and Volosin, J. S. 1993. Aquatic Ecological Risk. *Water Environment and Technology*, April.

CCME 2003. Linking water science to policy: Wastewater Treatment for Small Communities. *A CCME sponsored workshop*, February 11-12, Burlington, Ontario.

Chambers, P.A., Guy, M., Roberts, E.S., Charlton, M.N., Kent, R., Gagnon, C., Grove, G., and Foster, N. 2001. *Nutrients and their impact on the Canadian environment*. Agriculture and Agri- Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada and Natural Resources Canada. 241 p.

Cheung, C.W., Porter, J.F. and McKay, G. 2001. Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char. *Water Research* 35(3): 605-612.

Cheung, C.W., Porter, J.F. and McKay, G. 2002. Removal of Cu(II) and Zn(II) ions by sorption onto bone char using batch agitation. *Langmuir* 18(3), 650-656.

Chu, K. W., and Chow, K. L. 2002. Synergistic toxicity of multiple heavy metals is revealed by a biological assay using a nematode and its transgenic derivative. *Aquatic Toxicology* 61:53-64.

Chu, W. 1999. Lead metal removal by recycled alum sludge, *Water Research* 33(13): 3019-3025.

Chu, W. 2001. Dye removal from textile dye wastewater using recycled alum sludge. *Water research* 35(13):3147-3152.

Cleveland, L., Little, E. E., Hamilton, S. J., Buckler, D. R., and Hunn, J. B. 1986. Interactive toxicity of aluminum and acidity to early life stages of brook trout. *Transactions of American Fisheries Society* 115:610-620.

Cleveland, L., Buckler, D. R., and Brumbaugh, W. G. 1991. Residue dynamics and effects of aluminum on growth and mortality in brook trout. *Environmental Toxicology and Chemistry* 10: 243-248.

Comeau, Y., Brisson, J., Reville, J.P., Forget, C., and Drizo, A. 2001. Phosphorus removal from trout farm effluents by constructed wetlands. *Water Science and Technology* 44(11-12):55-60.

Committee Report 1972. Disposal of water treatment plant wastes. *Journal of American Water Works Association*, 64:814-820.

Commonwealth Technology Inc. 1999. *Wastewater treatment process alternative guide* [online]. http://www.ctienv.com/wwtguide.html [2003, 21 April].

Cooney, D.O. 1998. *Adsorption design for wastewater treatment*. Published by CRC press, Boca Raton, Florida, US, 190 p.

Cornwell, D.A., Mutter, R.N., and Vandermeyden, C. 2000. *Commercial Application and Marketing of Water Plant Residuals*. Published by AWWA Research Foundation, 183 p.

Crabtree, H.E., and Rowell, M.R. 1993. Standardisation of small wastewater treatment plants for rapid design and implementation. *Water Science and Technology* 28(10):17-24.

Crites R, and Tchobanoglous G. 1998. *Small and decentralized wastewater management systems*. Published by McGraw Hill, USA 1104 p.

Crittenden, J.C., Berrigan, J.K., and Hand, D.W. 1986. Design of the Rapid Small scale Adsorption Tests for a constant surface diffusivity. *Journal of Water Pollution Control Federation* 58(4): 312-319.

Crittenden, J.C., Berrigan, J.K., Hand, D.W., and Lykins, B. 1987. Design of Rapid Fixed Bed Adsorption Tests for non-constant diffusivities. *Journal of Environmental Engineering* 113(2): 243-259.

Cronan, C. S., and Reiners, W. A., Reynolds Jr., R. C., and Lang, G. E. 1978. Forest induced neurofibrillary degeneration, brain electrical activity and alterations in acquisition and retention. *Physiological Behaviour*, 10: 935-945.

Dayton, E.A., Basta, N.T., Jakober, C.A. and Hattey, J.A. 2003. Using treatment residuals to reduce phosphorus in agricultural runoff. *Journal of American Water Works Association* 95(4): 151-158.

Department of Justice, Canada 2004. *Pollutant substances pollution prevention regulations* [online]. http://laws.justice.gc.ca/en/s-9/c.r.c.-c.1458/52932.html [2004, 22 December]

DFO 1998. *Preliminary 1996 Canadian aquaculture production statistics* [online]. www.dfo-mpo.gc.ca/communic/statistics/aquacult/AQUA96.htm [2003, 25 August].

Diamadopoulos, E., and Vlachos, C. 1996. Coagulation-filtration of a secondary effluent by means of pre-hydrolized coagulants. *Water Science Technology* 33(10-11):193-201.

Dietze, A., GnirB, R., and Wiesmann, U. 2002. Phosphorus removal with membrane filtration for surface water treatment. *Water Science and Technology* 46(4-5): 257-264.

Dillon, P.J., Nicholls, K.H., Scheider, Y.N.D., and Jeffries, D.S. 1986. *Lakeshore Capacity Study. Trophic status.* Ontario Ministry of Municipal Affairs, Queen's Printer for Ontario.

Dittrich, J., Gnirss, R., Peter-Frohlich, A., and Sarfert, F. 1996. Microfiltration of municipal wastewater for disinfection and advanced phosphorus removal. *Water Science Technology* 34(9):125-131.

Dorfman, D. 1977. Tolerance of Fundulus heteroclitus to different metals in salt waters. *Bulletin of New Jersey Academy of Science*, 22(2):21-23.

Drizo, A., Comeau, Y., Forget, C., and Chapuis, R.P. 2002. Phosphorus saturation potential: a parameter for estimating the longevity of constructed wetland systems. *Environment Science and Technology*. 36:4642-4648.

Drndarski, N. D. 1979. Concentrations of metals in recent sediments as an indication of environmental pollution. *Bull. Soc. Chim. Beograd*, 44: 363-367.

EBS 2004. *Glossary* [online]. http://www.ebs.co.at/Englisch/inhalt/glossary.htm [2004, 12 August].

Eckenfelder, W.W. 1999. *Industrial Water Pollution Control*. Published by McGraw-Hill, USA, ISBN 0070393648, 600 p.

Environment Canada 1973a. *Use and production of iron salts for phosphorus removal*. Research report no. 5, Project no. 72-3-5.

Environment Canada 1973b. *Chemical dosing control for phosphorus removal*. Research report no. 4, project no. 72-5-11.

Environment Canada 1973c. *Utilization of industrial wastes and waste by-products for phosphorus removal: an inventory and assessment*. Research report no. 6, Project no. 72-3-5.

Environment Canada 1974. *Phosphorus removal study at the Sarnia WPCP*. Research report no. 14, Project no. 71-2-1.

Environment Canada 1976a. *Assessment of polyelectrolytes for phosphorus removal*. Research report no. 37, Project no. 72-5-6.

Environment Canada 1976b. *Phosphorus removal within existing wastewater treatment facilities*. Research report no. 44, project no. 71 - 1 - 1.

Environment Canada 1977. *Development of prediction models for chemical phosphorus removal: Volume I*. Research report no. 68, Project no. 73-3-9.

Environment Canada 1996. *Municipal water use database*. Ottawa, ON.

Environment Canada 2000. *Proposed Approach for Wastewater Effluent Quality – Final Report – June 1, 2000* [online]. www.ec.gc.ca/emsinfo/approach_e.htm [2004, 25 June].

Environment Canada 2001. *The state of municipal wastewater effluents in Canada*. Report prepared by Environmental conservation service. ISBN 0-662-29972-8.

Environmental Restoration Division 1999. *Bioaccumulation and bioconcentration screening* [online]. http://www.srs.gov/general/enviro/erd/ffa/rdh/p74.PDF [2002, 1 December].

Exley, C. 2000. Avoidance of aluminum by Rainbow Trout. *Environmental Toxicology and Chemistry* 19(4):933-939.

Fadali, O.A., Magdy, Y.H., Daifullah, A.A.M., Ebrahiem, E.E. and Nassar, M.M. 2004. Removal of chromium from tannery effluents by adsorption. *Journal of Environmental Science and Health., Part A* 39(2):465-472.

Faust, S. D., and Aly, O. M. 1999. *Chemistry of water treatment*. 2nd edition. Lewis Publishers, USA, ISBN 1575040115, 581 p.

France, R. L., and Stokes, P. M. 1987. Influence of manganese, calcium, and aluminum on hydrogen ion toxicity to the amphipod Hyalella azteca. *Canadian Journal of Zoology* 65:3071-3078.

Furukawa, K. and Fujita, M. 1993. Advanced treatment and food production by hydroponic type wastewater treatment plant. *Water Science and Technology*, 28(2):219-228.

Galarneau, E. and Gehr, R. 1997. Phosphorus removal from wastewaters: Experimental and theoretical support for alternative mechanisms. *Water Research* 31 (2), 328-338.

Gardner, M. J., Dixon, E., Sims, I., and Whitehouse, P. 2002. Importance of Speciation in Aquatic Toxicity Tests with Aluminum. *Bulletin of Environment Contamination and Toxicology* 68:195-200.

George, D.B., Berk, S. G., Adams, V. D., Morgan, E. L., Roberts, R. O., Holloway, C.A., Lott, R. C., Holt, L.K., Ting, R.S., and Welch, A.W. 1991. *Alum sludge in the aquatic environment*, AWWA Research Foundation Order Number 90582.

George, D.B., Berk, S.G., Adams, V.D., Ting, R.S., Roberts, R.O., Parks, L.H., and Lott, R.C. 1995. Toxicity of alum sludge extracts to a freshwater alga, protozoan, fish, and marine Bacterium. *Archives of Environmental contamination and toxicology* 29:149-158.

Gnirss, R., and Dittrich, J. 2000. Microfiltration of municipal wastewater for disinfection and advanced phosphorus removal: results from trials with different small scale pilot plants. *Water Environment Research* 72(5): 602-609.

Greaves, F.E., Thorp, B., and Critchley, R.F. 1990. Operational performance of package sewage treatment plants in North West England. *Water Science and Technology* 22(3-4):25-32.

Green, M.B., O'Connell, P.J., and Griffin, P. 1998. Uprating and rescuing small wastewater treatment facilities by adding tertiary treatment reed beds. *Water Environment Research* 70(7):1307-1317.

Guan, X, Shang, C., and Chen, G. 2005. Competitive adsorption of organic matter with phosphate on aluminum hydroxide. *Journal of Colloid and Interface Science*, in press.

Gutierrez, R., Delvasto, S., and Mesa, E. 1998. Problem of alum sludges disposal in Cali, Colombia. *Proceedings of the Fourteenth International Conference on Solid Waste Technology and Management*: Philadelphia, Pa, U.S.A., November 1-4.

Habs, H. 1997. *Aluminum*. Published by World Health Organization. Environmental health criteria: 194.

Hadjivassilis, I. 1990. Small sewage treatment plants and wastewater reuse in Cyprus. *Water Science and Technology* 22(3-4):9-16.

Halifax Regional Water Commission 2004. *Typical analysis of Pockwock/Lake Major water* [online]. http://www.hrwc.ns.ca/water_quality/analysis.pdf [2005, 15 September].

Hall, R. J., Likens, G. E., Fiance, S. B., and Hendrey, G. R. 1980. Experimental acidification of a stream in the Hubbard Brook Experimental Forest, New Hampshire. *Ecology*, 61: 976-989.

Haron, M. J., Wasay, S. A., and Tokunaga, S. 1997. Preparation of basic Yttrium carbonate for phosphate removal. *Water Environment Research* 69(5):1047-1051.

Harper, T., and Rosenberg, A. 1995. Polyaluminum chloride: an alternative to conventional coagulants. *World Water and Environmental Engineering* 9:15.

Havas, M. 1986. *Effects of aluminum on aquatic biota*. In: Havas, M.and J. F. Jaworski (Eds.), *Aluminum in the Canadian Environment*, National Research Council of Canada, Associate Committee on Scientific Criteria for Environmental Quality, pp 79-127

Havens, K. E. 1990. Aluminum binding to ion exchange sites in acid-sensitive versus acid-tolerant cladocerans. *Environment Pollution* 64:133-141.

Havens, K. E. 1993. Acid and aluminum effects on the survival of littoral macro-invertebrates during acute bioassays. *Environment Pollution* 80:95-100.

Hillis, P. 2000. *Membrane technology in water and wastewater treatment*. Special publication, Royal Society of Chemistry.

Holtze, K.E., and Hutchinson, N.J. 1989. Lethality of low pH and Al to early life stages of six fish species inhabiting Precambrian Shield waters in Ontario. *Canadian Journal of Fisheries and Aquatic Science* 46: 1188.1202.

Hu, Z., and Gagnon, G.A. 2005. New types of filter media for recirculating bio-filters. Presented at the *2005 Annual Technical Symposium of Water Environment Association* of Ontario, Huntsville.

Huang, S-H. and Chiswell, B. 2000. Phosphate removal from wastewater using spent alum sludge. *Water Science Technology* 42(3-4): 295-300.

Hutcheson, M.S., and Odense, R. B. 1984. *A study of the toxicity mechanisms to Atlantic salmon of acidic lake waters with high aluminum concentrations*. Atlantic Oceanic Co. Ltd. Dartmouth. 17 p.

Hutchinson, N. J. and Sprague, J. B. 1986. Toxicity of trace metal mixtures to American flagfish (Jordanella floridae) in soft, acidic water and implications for cultural acidification. *Canadian Journal of Fisheries and Aquatic Science* 43:647-655.

Industry Canada 1997. *Bear River Solar Aquatics* [online]. http://collections.ic.gc.ca/western/bearriver.html [2003, 31 August].

Ioannou, A. and Dimirkou, A. 1997. Phosphate adsorption on hematite, kaolinite, and kaolinite-hematite (k-h) systems as described by a constant capacitance model. *Journal of Colloid and Interface Science* 192:119-128.

Iwai, S., Oshino, Y., and Tsukada, T. 1990. Design and operation of small wastewater treatment plants by the microbial film process. *Water Science and Technology* 22(3-4):139-144.

Jansen, J.C., Pedersen, B.M., and Moldt, E. 1993. Evaluation of small wastewater treatment plants in the county of Arhus – Denmark. *Water Science and Technology* 28(10):33-41

Jiang, J., and Graham, N.J.D. 1998. Pre-polymerised inorganic coagulants and phosphorus removal by coagulation – A review. *Water SA* 24(3):237-244.

Johansson, L. 1997. The use of LECA (Light Expanded Clay Aggregates) for the removal of phosphorus from wastewater. *Water Science and Technology* 35(5): 87-93.

Johansson L. 1999a. Industrial by-products and natural substrata as phosphorus sorbents. *Environment Technology* 20:309-316.

Johansson L. 1999b. Blast furnace slag as phosphorus sorbents – column studies. *Science of the Total Environment* 229:89-97.

Johansson, L. and Gustafsson, J.P. 2000. Phosphate removal using blast furnace slags and opoka-mechanisms. *Water Research* 34(1):259-265.

Jokela, P., Ihalainen, E., Heinanen, J., and Viitasaari, M. 2001. Dissolved air flotation treatment of concentrated fish farming wastewaters, *Water Science and Technology* 43(8):1115-1121.

Jonasson, B. 1996. Phosphorus transformations in alum sludge amended soils, *Swedish Journal of Agricultural Research* 26(2):69.

Jonsson, L., Plaza, E., and Hultman, B. 1997. Experiences of nitrogen and phosphorus removal in deep-bed filters in the Stockholm area, *Water Science and Technology* 36(1):183-190.

Kato, Y., Nakai, T., Sato, Y., Takahashi, N., and Matsuoka, I. 1993. Removal of phosphorus in wastewaters by flotation method, *Proceedings of the 1ˢᵗ International Conference on Processing Materials for Properties*, pp. 109-112.

Kemp, A. L. W., Williams, J. D. H., Thomas, R. L., and Gregory, M. L., 1978. Impact of man's activities on the chemical composition of the sediments of lakes Superior and Huron. *Water Air and Soil Pollution* 10: 381-402.

Kibria, G., Nugegoda, D., Lam, P., and Fairclough, R. 1996. *Aspects of phosphorus pollution in aquaculture* [online]. http://www.csa.com/hottopics/aquacult/biblio40.html [2003, 25 August].

Kim, J.G., Kim, J.H., Moon, H-S., Chon, C-M. and Ahn, J.S. 2003a. Removal capacity of water plant alum sludge for phosphorus in aqueous solutions. *Chemical Speciation and Bioavailability* 14, 67-73.

Kim, S., Woo, S., Cheong, E., and Ahn, T. 2003b. Nutrient removal from sewage by an artificial food web system composed of phytoplankton and Daphnia magna. *Ecological Engineering*, 21:249-258.

Klute, A. 1986. *Methods of Soil Analysis Part1: Physical and Mineralogical Methods*. 2nd Edition. Published by American Society of Agronomy.

Landis, W. G., and Yu, M. 1999. *Introduction to Environmental Toxicology*. 2nd edition, published by Lewis Publishers, USA, ASIN:1566702658, 390 p.

Laughton, P.J., Papadopol, C.S., and Jaciw, P. 1990. Zero discharge through innovative applicatioin of intensive silviculture to effluent disposal from a small Canadian wastewater treatment plant. *Water Science and Technology* 22(3-4):217-224.

Lefevere, G. 2004. In situ Fourier-transform infrared spectroscopy studies of inorganic ions adsorption on metal oxides and hydroxides. *Advances in Colloid and Interface Science* 107:109–123

Liberti, L., Petruzzelli, D., and Florio, L. D. 2001. REM NUT Ion Exchange plus Struvite Precipitation Process. *Environmental Technology* 22(11):1313-1324.

Louzeiro, N.R., Mavinic, D.S., Oldham, W.K., Meisen, A., and Gardner, I.S. 2002. Methanol-induced biological nutrient removal kinetics in a full-scale sequencing batch reactor. *Water Research* 36(11):2721-2732.

Lozier, J.C., Jones, G., and Bellamy, W. 1997. Integrated membrane treatment in Alaska. *Journal of American Water Works Association* 89(10):50-64.

Lucas, J. B, Kupar, J., Novak, J. L., Knocke, W. R., Reneau, R. B., and Dilhara, T. A. 1991. Impacts of land application of alum sludge on the growth of tall fescue and loblolly pines, Proceedings – *AWWA Annual Conference*, p 745-756.

Lucas, J. B., Dillaha, T. A., Reneau, R. B., Novak, J. T., and Knocke, W. R. 1994. Alum sludge land application and its effect on plant growth. *Journal of American Water Works Association* 86(11):75-83.

Makris, K.C., Harris, W.G., O'Connor, G.A., Obreza, T.A., and Elliott, H.A. 2005a. Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals. *Environmental Science and Technology* 39:4280-4289.

Makris, K.C., Harris, W.G., O'Connor, G.A., and El-Shall, H. 2005b. Long-term phosphorus effects on evolving physicochemical properties of iron and aluminum hydroxides. *Journal of Colloid and Interface Science* 287:552-560.

Malmer, N. 1976. Acid precipitation: chemical changes in the soil. Ambio 5: 231-234.
Mander, U., and Mauring, T. 1997. Constructed wetlands for wastewater treatment in Estonia. *Water Science and Technology*, 35(5):323-330.

Mann, R.A., and Bavor, H.J. 1993. Phosphorus removal in constructed wetlands using gravel and industrial waste substrata. *Water Science Technology* 27(1):107-113.

Mann, R.A. 1996. *Phosphorus removal by constructed wetlands: substratum adsorption.* Ph.D. thesis, Department of Environmental Science, University of Western Sidney, Haukesbury, Australia.

Mant, C., Peterkin, J., May, E., and Butler, J. 2003. A feasibility study of salix viminalis gravel hydroponic system to renovate primary settled water. *Bioresource Technology*, 90:19-25.

Mars, R., Taplin, R., Ho, G., and Mathew, K. 2003. Greywater treatment with the submergent *Triglochin huegelii*-a comparison between surface and subsurface systems. *Ecological Engineering* 20:147-156.

Mayer, F.L. Jr., and Ellerseick, M. R. 1986 *Manual of Acute Toxicity: Interpretation and Data Base for 410 Chemical and 66 Species of Freshwater Animals.* U.S.F.W.S. Resource Publication #160.

Metcalf and Eddy Inc., 2003. *Wastewater Engineering: treatment and reuse.* Published by McgrawHill, New York, USA, 1819 p.

Mikhail, S., Zaki, T. and Khalil, L. 2002. Desulfurization by an economically adsorption technique. *Applied Catalysis*, A 227 (1-2), 265-278.

Mitsch, W.J. and J.G. Gosselink. 2000.*Wetlands*, 3rd Ed. John Wiley & Sons, New York. 920 pp.

Narasiah, K.S., Morasse, C. and J. Lemay 1994. Phosphorus removal from aerated lagoons using alum, ferric chloride and lime. *Water pollution research journal of Canada* 28(1):1-18.

Nassar, M. M., Daifullah, A.E.A., Magdy, Y.H. and Ebrahiem, E.E. 2002. Uptake of cationic dyes by cement kiln dust: Sorption mechanism and equilibrium isotherm. *Adsorption Science and Technology* 20(7):657-668.

Nnadi, F.N., and Addasi, D. 1999. Estimating phosphorus removal in lakes using marsh wetlands. *Journal of Environmental Science Health, Part A: Toxic/Hazardous Substances and Environment Engineering* 34(2):405-422.

Nova Scotia Department of Natural Resources 1993. *Limestone and dolomite in Nova Scotia* [online]. http://www.gov.ns.ca/natr/meb/ic/ic13.htm [2004, 23 September].

Nowack, B. 2003. Environmental chemistry of phosphonates. *Water Research* 37:2533-2546.

Nutt, S.G. 1991. A review of approaches to achieve low effluents phosphorus concentrations. *Water pollution research Journal of Canada* 26(4): 495-547.

Odegaard, H., and Storhaug, R. 1990. Small wastewater treatment plants in Norway. *Water Science and Technology* 22(3-4):33-40.

Odegaard, H., Rusten, B., and Badin, H. 1993. Small wastewater treatment plants based on moving bed biofilm reactors. *Water Science and Technology* 28(10):351-359.

Olesen, N.S. 1990. Nutrient removal in small wastewater treatment plants. *Water Science and Technology*, 22(3-4):211-216.

Parida, K.M. and Mohanty, S. 1998. Studies on Indian Ocean manganese nodules. VIII. Adsorption of aqueous phosphate on ferromanganese nodules. *Journal of Colloid Interface Science* 199:22-27.

Park, J. K., Wang, J., and Novotny, G. 1997. *Wastewater Characteristization for Evaluation of Biological Phosphorus Removal. Research report 174, Wisconsin Department of Natural Resources* [online]. http://www.dnr.state.wi.us/org/water/wm/ww/biophos/abstract.htm [2003, 3 February].

Penetra, R. G., Reali, M. A. P., Foresti, E., and Campos, J. R. 1999. Effluent Post-treatment – Post-treatment of effluents from anaerobic reactor treating domestic sewage by dissolved air flotation, *Water Science and Technology* 40(8):137-144.

Petrich, S. M., and Reish, D. J. 1979. Effects of aluminum and nickel on survival and reproduction in polychaetous annelids. *Bulletin of Environment Contamination and Toxicology* 23:698-702.

Pradhan, J., Das, J., Das, S. and Thakur, R.S. 1998. Adsorption of phosphate from aqueous solution using activated red mud. *Journal of Colloid and Interface Science* 204:169-172.

Rababah, A.A., and Ashbolt, N.J. 2000. Innovative production treatment hydroponic farm for primary municipal sewage utilization. *Water Research*, 34(3):825-834.

Racault, Y., and Vachon, A. 1990. Sewage treatment for small local authorities: choice of process and recent trends in France. *Water Science and Technology* 22(3-4):17-24.

Ramamoorthy, S. 1988. Effect of pH on speciation and toxicity of aluminum to Rainbow trout (Salmo gairdneri). *Canadian journal of fisheries and aquatic science*, 45: 634-642.

Randall, C. W., Barnard, J. L. and Stensel, H.D. 1992. *Design and retrofit of wastewater treatment plants for biological nutrient removal*. Pennsylvania: Technomic Publishing Company, Inc.

Ratanatamskul, C., CHiemchaisri, C., and Yamamoto, K. 1995. The use of zeolite-iron column for residual ammonia and phosphorus removal in the effluent from a membrane process as an on-site small-scale domestic wastewater treatment. *Water Science and Technology* 31(9):145-152.

Rectenwald, L.L., and Drenner, R.W. 2000. Nutrient removal from wastewater effluent using an ecological water treatment system. *Environment Science Technology* 34:522-526.

Rismal, M. 1990. The experience and the results of operating small wastewater treatment plants. *Water science and Technology* 22(3-4):267-273.

Robertson, W.D., Schiff, S.L., and Ptacek, C.J. 1998. Review of phosphate mobility and persistence in 10 septic system plumes. *Groundwater* 36:1000-1010.

Rogalla, F., Roudon, G., Sibony, J., and Blondeau, F. 1992. Minimizing nuisances by covering compact sewage treatment plants, *Water Science and Technology* 25(4-5):363-374.

Rosseland, B. O., and Skogheim, O. K. 1984. *A comparative study on salmonid fish species in acid aluminum-rich water. II. Physiological stress and mortality of one- and two year old fish*. Oslo, Norway, Institute of Fresh Water Ecology, pp 186-194.

Roy, M., and Couillard, D. 1998. Metal leaching following sludge application to a deciduous forest soil. *Water Research*, 32(5):1642-1652.

Rubin, A. J., and Blocksidge, H. 1979. Coagulation of montmorillonite suspensions with aluminum sulfate. *Journal of American Water Works Association* 71:102-109.

Rusten, B., and Eliassen, H. 1993. Sequencing batch reactors for nutrient removal at small wastewater treatment plants. *Water Science and Technology* 28(10):233-242.

Sakadevan, K., and Bavor, H.J. 1998. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. *Water Research* 32 (2): 393-399.

Schindler, D. W., Wagemann, R., Cook, R. B., Ruszczynski, T., and Prokopowich, J. 1980. Experimental acidification of Lake 223, Experimental Lakes Area: background data and the first three years of acidification. *Canadian Journal of Fisheries and Aquatic Science* 37:342-354.

Serodes, J.B., and Normand, D. 1999. Phosphorus removal in agricultural wastewater by a recently constructed wetland. *Canadian Journal of Civil Engineering* 26(3):305-311.

Sherman, J. J., Van Horn, H. H., and Nordstedt, R. A. 2000. Use of flocculants in dairy wastewaters to remove phosphorus, *Applied Engineering in Agriculture* 16(4):445-452.

Skogheim, O. K., and Rosseland, B. O. 1986. Mortality of smolt of Atlantic salmon, Salmo salar L., at low levels of aluminum in acidic softwater. *Bulletin of Environment Contamination and Toxicology* 37:258-265.

Skogheim, O. K., Rosseland, B. O., and Sevaldrud, I. H. 1984. *Deaths of spawners of Atlantic salmon (Salmo salar L.) in River Ogna, SW Norway, caused by acidified aluminum-rich water. Oslo, Norway*, Institute of Fresh Water Ecology, pp 195-202 (Research Report No. 61).

Smith, M.L. and Campbell, C.E. 2000. Effect of cement kiln dust on pH and phosphorus concentrations in an activated sludge wastewater treatment system. *Water Quality Research Journal of Canada* 35(2):299-311.

Soto, F., Garcia, M., De Luis, E., and Becares, E. 1999. Role of Scirpus lacustris in bacterial and nutrient removal from wastewater. *Water Science Technology*. 40(3):241-247.

Soucek, D. J., Cherry, D. S., and Zipper, C. E. 2001. Aluminum-dominated acute toxicity to the Cladoceran Ceriodaphnia dubia in neutral waters downstream of an acid mine drainage discharge. *Canadian Journal of Fisheries and Aquatic Science* 58:2396-2404.

Spencer, R. 1990. Solar aquatic treatment of septage. *Biocycle,* 31(5):66-70.

Stephens, J.C. 1998. Factors limiting the acceptance and use of innovative environmental technologies: a case study of the solar aquatics system (SAS) technology for wastewater treatment. *Journal of Environmental Systems* 26(2):163-170.

Stokes, P. M., and Hutchinson, T. C. 1976. The effects of acid and particulate precipitation on phytoplankton and lake chemistry in the Sudbury Region of Ontario, Canada. *Proc. Int. Symp. Acid Precipitation and the Forest Ecosystem,* 1: 499-500.

Sujana, M.G., Thakur, R. S., and Rao, S. B. 1998. Removal of fluoride from aqueous solution by using alum sludge. *Journal of Colloid and Interface Science* 206 (1), 94.

SYSCO. 2004. *Slag analysis – chemical* [online].
http://www.sysco.ns.ca/slag/slag_analysis_chemical.htm [2004 23 September].

Tandjung, S. D. 1982. *The acute toxicity and histopathology of Brook Trout (Salvelinus Fontinalis, Mitchill) exposed to aluminum in acid water*. Ph.D. thesis. Fordham University, New York City, USA.

Teal, J.M., and Peterson, S.B., 1993. Solar aquatic system septage treatment plant. *Environmental Science and Technology*, 27(1):34-37.

Theis, T.L., and Fromm, G.A. 1977. Phosphate removal using waste calcium sulfate, *Journal of environmental engineering* 103(5).

Tyagi, R.D., Coullard, D., and Tran, F.T. 1990. Studies on microbial leaching of heavy metals from municipal sludge. *Water Science and Technology*, 22(12):229-238.

USEPA 1992. *Method 1311: Toxicity Characteristics Leaching Procedure* [online]. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/1311.pdf [2005, 22 September].

USEPA 1999a. *Biosolids Generation, Use, and Disposal in The United States*. EPA530-R-99-009.

USEPA. 1999b. *Guidance manual for enhanced coagulation and enhanced precipitation softening* [online]. www.epa.gov/safewater/mdbp/coaguide.pdf [2003, 16 August].

USEPA 2000. *Environmental assessment for the final effluent limitations guidelines, pre-treatment standards for new and existing sources and new source performance standards for the centralized waste treatment* [online].
http://www.epa.gov/ost/guide/cwt/final/envlass.html [2005, 13 November 13].

USEPA 2004. *Effluent limitations guidelines and new source performance standards for the concentrated aquatic animal production point source category; final rule*. 40 DFR Part 451.

Vaillant N, Monnet F, Sallanon H, Coudret A, and Hitmi A. 2003. Treatment of domestic wastewater by an hydroponic NFT system. *Chemosphere* 50(1):121-129

Wallen, I. E., Greer, W. C., and Lasater, R. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. *Sew Ind Wastes*, 29:695-711.

Wang, M.C., Hull, J.Q., Jao, M., Dempsey, B.A., and Cornwell, D.A. 1992. Engineering behavior of water treatment sludge. *Journal of Environmental Engineering* 118(6):848-864.

Wang, F., Coullard, D., Auclair, J., and Campbell, P. G. C. 1998. Effects of alum-treated waste water sludge on barley growth, *Water, Air and Soil Pollution* 108(1-2):33-49.

Wareham, D.G., Hall, K.J., and Mavinic, D.S. 1995. ORP screening protocol for biological phosphorus removal in sequencing batch reactors. *Canadian Journal of Civil Engineering* 22(2):260-269.

Wicklung Glynn, A., Norrgren, L., and Malmborg, O. 1992. The influence of calcium and humic substances on aluminum accumulation and toxicity in the minnow, Phoxinus phoxinus, at low pH. *Comp Biochemistry Physiology*, 102C(3):427-432.

Wilson, R. W., Bergman, H. L., and Wood, C. M. 1994. Metabolic costs and physiological consequences of acclimation to aluminum in juvenile rainbow trout (Oncorhynchus mykiss). 1: Acclimation specificity, resting physiology, feeding, and growth. *Canadian Journal of Fisheries and Aquatic Science* 51:527-535.

Xie, W., Kondo, M., and Naito, Y. 1994. Study on phosphorus removal using a new coagulation system, *Water Science and Technology* 30(6):257-262.

Yamada, H., Kayama, M., Saito, K., and Hara, M. 1986. A fundamental research on phosphate removal by using slag. *Water Research* 22(5):547-557.

Yannai, S., Makady, S., Sachs, K. and Berk, Z. 1978. The safety of several algae grown on wastewater as a feedstuff for broilers. *Ergebn. Limnology* 11:139-149.

Young, D.F. and Koopman, B. 1991. Electricity use in small wastewater treatment plants. *Journal of Environmental Engineering*, 117(3): 300-307.

Yu, K. C., Chang, J. S., Chen, I. P., Chang, D. J., Chang, C. Y., and Chen, S. H. 2000. Removal of colloid and dissolved phosphorus by coagulation and membrane microfiltration, *Journal of Environmental Science and Health, Part A,* 35(9):1603-1616.

Zeghal, S., Puznava, N., Subra, J. P., and Sauvegrain, P. 1998. Process control for nutrient removal using lamella sedimentation and floating media filtration, *Water Science and Technology* 38(3):227-235.

Zhang, X., Feagley, S.E., Day, J.W., Conner, W.H., Hesse, I.D., Rybczyk, J.M., and Hudnall, W.H. 2000. Water chemistry assessment of wastewater remediation in a natural swamp. *Journal of environmental quality*, 29(6):1960-1968

Zhao, D. and Sengupta, A. K. 1998. Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers, *Water Research* 32(5):1613-1625.

Zhao, Y.Q., and Bache, D.H. 2001. Conditioning of alum sludge with polymer and gypsum. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 194(1-3): 213-220.

APPENDIX A: EXPERIMENTAL RESULTS OF BATCH TESTS

Experimental Results on Variation of pH, Initial Phosphorus Concentration and Particle Size

Phosphorus concentration

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	2.3	2.35	2.6	2.35	2.35	2.4	2.3	2.45	2.6
4	0.11	0.06	0.22	0.02	0.03	0.14	0.07	0.02	0.86
8	0.04	0.06	0.09	0.01	0.02	0.04	0.01	0.03	0.15
12	0.03	0.28	0.05	0.03	0.02	0.02	0.1	0.05	0.13
16	0.01	0.28	0.07	0.02	0.09	0.02	0.01	0.08	0.04

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	10.8	9.6	10.6	11.4	11.6	10.2	15.6	10.4	11
8	0.2	0.64	0.8	0.09	0.32	0.4	0.06	0.68	4.8
16	0.45	0.24	0.26	0.08	0.16	0.09	0.03	0.23	2.8
24	0.06	0.03	0.15	0.09	0.06	0.05	0.05	0.22	0.4
32	0.21	0.14	0.16	0.07	0.11	0.04	0.17	0.21	0.2

Phosphorus removal (%)

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
4	95.22	97.45	91.54	99.15	98.72	94.17	96.96	99.18	66.92
8	98.26	97.45	96.54	99.57	99.15	98.33	99.57	98.78	94.23
12	98.70	88.09	98.08	98.72	99.15	99.17	95.65	97.96	95.00
16	99.57	88.09	97.31	99.15	96.17	99.17	99.57	96.73	98.46

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
8	98.15	93.33	92.45	99.21	97.24	96.08	99.62	93.46	56.36
16	95.83	97.50	97.55	99.30	98.62	99.12	99.81	97.79	74.55
24	99.44	99.69	98.58	99.21	99.48	99.51	99.68	97.88	96.36
32	98.06	98.54	98.49	99.39	99.05	99.61	98.91	97.98	98.18

pH

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	3.01	2.83	2.88	4.95	5.01	4.87	6.87	7.11	6.97
4	3.32	3.29	3.59	4.11	4.21	4.28	6.98	7.05	7.09
8	3.59	3.75	3.72	4.69	4.59	4.65	6.93	6.57	6.83
12	4.01	4.43	4.21	4.58	4.68	4.64	6.68	6.75	6.61
16	4.59	4.53	4.56	4.88	4.79	4.71	6.61	6.54	6.57

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	3.05	3.25	3.53	5.11	5.08	4.91	6.95	6.89	7.09
8	3.54	3.78	3.86	4.21	4.25	4.16	7.04	6.95	7.12
16	3.98	4.16	4.19	4.53	4.55	4.62	6.81	6.75	6.89
24	4.15	4.39	4.39	4.61	4.84	4.89	6.56	6.78	6.51
32	4.29	4.42	4.31	4.98	4.98	5.09	6.61	6.57	6.48

Effluent temperature (^{0}C)

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	20.3	20.1	20.3	20.1	20	20.1	19.9	20	20.1
4	20.1	20.3	20.2	20.1	20.1	20	19.9	20.1	20.2
8	20.2	20.2	20.1	20	19.9	20.2	20	19.9	20
12	20.2	20.1	20.2	19.9	20	20.1	20	19.9	20.1
16	20.3	20.1	20.3	20	20.1	20.1	20.1	20	20

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	20.4	20.2	20.2	20	20.1	20.1	20.1	19.9	20
8	20.3	20.1	20.2	19.9	20.1	20.1	20.1	20	20
16	20.3	20.2	20.3	19.9	20.1	20.2	20	20.1	20
24	20.2	20.2	20.4	20.1	20	20.2	19.9	20	20.1
32	20.2	20.3	20.4	20	20.1	20.1	20	20	20.1

Duplicate Experimental Results on Variation of pH, Initial Phosphorus Concentration and Particle Size

Phosphorus concentration

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	2.4	2.45	2.6	2.45	2.5	2.4	2.4	2.55	2.5
4	0.13	0.32	0.52	0.05	0.13	0.18	0.07	0.09	0.27
8	0.05	0.21	0.39	0.02	0.05	0.09	0.08	0.1	0.15
12	0	0.15	0.25	0.03	0.07	0.1	0.02	0.08	0.1
16	0	0.05	0.09	0.01	0.02	0.06	0	0.05	0.07

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	10.3	9.8	10.1	10.4	10.6	10.2	10.8	10.2	11.1
8	0.41	0.68	0.83	0.09	0.38	0.63	0.18	0.49	1.8
16	0.21	0.24	0.45	0.08	0.29	0.39	0.11	0.28	1.6
24	0.2	0.3	0.38	0.09	0.16	0.15	0.15	0.11	0.6
32	0.06	0.14	0.19	0.07	0.11	0.19	0.09	0.18	0.26

Phosphorus removal (%)

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
4	94.58	86.94	80.00	97.96	94.80	92.50	97.08	96.47	89.20
8	97.92	91.43	85.00	99.18	98.00	96.25	96.67	96.08	94.00
12	100.00	93.88	90.38	98.78	97.20	95.83	99.17	96.86	96.00
16	100.00	97.96	96.54	99.59	99.20	97.50	100.00	98.04	97.20

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
8	96.02	93.06	91.78	99.13	96.42	93.82	98.33	95.20	83.78
16	97.96	97.55	95.54	99.23	97.26	96.18	98.98	97.25	85.59
24	98.06	96.94	96.24	99.13	98.49	98.53	98.61	98.92	94.59
32	99.42	98.57	98.12	99.33	98.96	98.14	99.17	98.24	97.66

pH

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	3.11	3.09	2.81	5.04	4.8	4.8	7.04	7.1	6.82
4	3.91	3.82	3.99	4.49	4.2	4.22	7.11	7.08	7.02
8	4.36	4.18	4.22	4.68	4.72	4.85	6.81	6.84	6.61
12	4.46	4.31	4.29	4.89	4.85	4.61	6.78	6.68	6.46
16	4.55	4.37	4	5.11	5.29	4.7	6.54	6.56	6.33

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	2.98	3.08	3.12	5.04	5.11	5.19	7.08	7.11	7.06
8	3.27	3.57	3.56	4.26	4.11	4.29	7.05	7.25	7.1
16	3.87	4.01	3.89	4.39	4.25	4.61	6.75	6.98	6.9
24	4.49	4.55	4.34	4.89	4.75	4.81	6.68	6.57	6.55
32	4.67	4.46	4.56	5.08	4.98	5.07	6.72	6.61	6.42

Effluent temperature (^{0}C)

Influent P = 2.5 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	20.4	20.3	20.5	20.3	20.3	20.4	20.4	20.4	20.4
4	20.3	20.3	20.5	20.4	20.3	20.4	20.4	20.4	20.4
8	20.3	20.4	20.5	20.3	20.4	20.5	20.3	20.4	20.4
12	20.4	20.4	20.5	20.5	20.4	20.5	20.4	20.5	20.4
16	20.3	20.5	20.6	20.3	20.5	20.6	20.5	20.6	20.5

Influent P = 10 mg/L

ODS (g/L)	pH = 3			pH = 5			pH = 7		
	Different particle sizes (μm)								
	250	425	1180	250	425	1180	250	425	1180
0	20.4	20.4	20.3	20.4	20.4	20.3	20.3	20.4	20.3
8	20.4	20.2	20.2	20.5	20.5	20.4	20.3	20.5	20.4
16	20.4	20.5	20.4	20.4	20.6	20.3	20.4	20.3	20.5
24	20.3	20.3	20.3	20.3	20.4	20.3	20.3	20.4	20.3
32	20.5	20.4	20.3	20.5	20.4	20.4	20.5	20.4	20.3

APPENDIX B: EXPERIMENTAL RESULTS OF RSSCT COLUMN TESTS

Operating Condition for Experiments Conducted on pH and Initial Phosphorus

Porosity

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Blank (B) (g)	68.1	68	67.6	67.8	67.9	68
B+Dry samples (g)	169.5	169.6	166.2	169.1	164.2	167
B+Wet samples (g)	228.9	227.1	221.4	225.4	221.5	218.8
Porosity	0.594	0.575	0.552	0.563	0.573	0.518

Flow rate (mL/min)

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Beginning	2.1	2.4	2.2	2.4	2	2.2
Middle	2.1	2.4	2.2	2.4	1.8	2.1
End	2.2	2.5	2.2	2.4	2	2
Average	2.133333	2.433333	2.2	2.4	1.933333	2.1

Operating variables

	Column1	Column2	Column3	Column4	Column5	Column6
pH	7	7	5	5	3	3
Initial P (mg/L)	2.5	10	2.5	10	2.5	10
Particle size (mm)	0.98	0.98	0.98	0.98	0.98	0.98
Porosity	0.594	0.575	0.552	0.563	0.573	0.518
Flowrate (mL/min)	2.13333	2.43333	2.2	2.4	1.933333	2.1

Effluent Phosphorus Concentration (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	0.06	0.01	0.01	0.04	0.04	0.04
3.5	0.05	0.05	0.04	0.05	0.03	0.06
7.5	0.06	0.07	0.03	0.09	0.07	0.09
15.5	0.09	0.09	0.05	0.07	0.09	0.08
19.5	0.07	0.09	0.05	0.09	0.08	0.09
23.5	0.09	0.7	0.07	0.09	0.09	0.41
29	0.25	1.8	0.05	0.57	0.2	0.97
31.3	0.35	2.1	0.02	1.7	0.3	1.2
39.3	0.45	3.2	0	3.1	0.3	1.7
52.3	0.5	4.1	0.05	4.2	0.3	2
63.3	0.65	5.6	0.1	5.8	0.3	2
76.3	0.7	5.8	0.2	5.9	0.35	2.4
89.3	0.85	6.8	0.9	6.2	0.25	2.7
99.3	0.9	7	1.1	6	0.4	2.9
112.8	0.95	7.6	1.1	8.6	0.45	2.8
136.8	1.18	6.4	1.25	6.6	0.45	3
160.8	1.25	8.6	1.5	7.6	0.55	4.1
185.3	1.25		2.5		2.5	4.1

Effluent pH

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	5.67	5.68	4.79	4.91	3.16	4.09
3.5	5.39	5.37	4.38	4.51	3.44	3.81
7.5	5.37	5.27	4.57	4.12	3.88	3.9
15.5	5.4	5.43	4.53	4.31	3.84	3.75
19.5	5.36	5.49	4.53	4.31	3.83	3.74
23.5	5.35	5.55	4.56	4.42	3.81	3.73
29	5.54	5.77	4.63	4.6	3.8	3.69
31.3	5.68	5.95	4.7	4.67	3.77	3.68
39.3	5.85	6.07	4.86	4.66	3.73	3.69
52.3	6	6.23	4.99	4.53	3.73	3.64
63.3	6.12	6.44	5.16	4.79	3.7	3.61
76.3	6.15	6.21	5.31	5.06	3.65	3.52
89.3	6.12	6.23	5.9	5.68	3.56	3.49
99.3	6.1	6.29	6.19	6.06	3.49	3.34
112.8	6.19	6.31	6.27	6.29	3.54	3.44
136.8	6.26	6.46	6.46	6.55	3.5	3.33
160.8	6.43	6.51	6.53	6.47	3.41	3.33
185.3	6.47		6.69		3.41	3.21

Effluent Temperature (^{0}C)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	19.9	20	20	20.2	20.2	20.2
3.5	19.8	19.7	19.7	19.7	19.6	19.6
7.5	19.6	19.6	19.4	19.4	19.3	19.4
15.5	20.1	20.3	20.7	20.4	20.2	20
19.5	20.8	20.7	20.7	20.7	20.7	20.5
23.5	20.7	20.6	20.4	20.4	20.5	20.4
29	20.1	20.1	20.1	20.2	20.1	20.1
31.3	19.8	19.7	19.6	19.8	19.8	19.8
39.3	21.1	21.1	21.2	21.2	21.4	21.4
52.3	20.5	20.4	20.4	20.4	20.4	20.3
63.3	21	21	21.2	21.1	21.3	21.2
76.3	20.6	20.6	21	20.7	21	20.8
89.3	20.6	21	21.3	20.9	21.1	20.7
99.3	21.3	21.4	21.5	21.3	21.4	21.2
112.8	21.8	21.8	21.6	21.3	21.4	21.3
136.8	23	23.1	23.1	23	23.1	23.67
160.8	19.6	19.6	19.6	19.9	19.9	19.9
185.3	19.6		19.1		19.2	19.1

Effluent Soluble Aluminum (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	1.4	1.425	1.05	0.675	0.725	0.675
7.5	0.3	0.1	1.75	0.325	22.5	22.5
19.5	0.3	0.025	1.825	0.15	25	30.15
29	0.3	0.275	1.35	0.225	29.25	30.25
39.3	0.15	0.1	1.225	0.175	29.45	24.55
63.3	0.125	0.275	0.975	0.175	29.15	26.3
89.3	0.1	0.25	0.45	0.1	30.15	22.95
112.8	0.3	0.025	0.25	0.2	30.6	26.4
136.8	0.375	0.125	0.25	0.075	30.75	28.05
160.8	0.4	0.15	0.2	0.1	31.65	28.9

Effluent BOD$_5$ (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	15	27	30	18	15	21
7.5	6	12	24	24	27	21
19.5	10	0	0	0	0	0
29	21	12	24	15	21	18
39.3	15	27	12	15	21	18
63.3	6	18	24	21	27	33
89.3	18	24	24	30	27	0
112.8	6	27	15	24	15	30
136.8	24	21	27	33	3	0
160.8	6	6	30	33	0	3

Operating Condition for Duplicate Experiments Conducted on pH and Initial

Phosphorus

Porosity

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Blank (B) (g)	68	68.1	67.8	67.5	67.6	68.1
B+Dry samples (g)	169.6	169.5	166.1	169.3	164.1	167.1
B+Wet samples (g)	228.7	227.3	221.5	225.5	221.4	218.6
Porosity	0.591	0.578	0.554	0.562	0.573	0.515

Flow rate (mL/min)

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Beginning	2.1	2.4	2.2	2.4	2	2.2
End	2.2	2.5	2.2	2.4	2	2
Average	2.15	2.45	2.2	2.4	2	2.1

Operating variables

	Column1	Column2	Column3	Column4	Column5	Column6
pH	3	5	7	3	5	7
Initial P (mg/L)	2.5	2.5	2.5	10	10	10
Particle size (mm)	0.98	0.98	0.98	0.98	0.98	0.98
Porosity	0.591	0.578	0.554	0.562	0.573	0.515
Flowrate (mL/min)	2.15	2.45	2.2	2.4	2	2.1

Effluent Phosphorus Concentration (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	0.01	0.03	0.06	0.05	0.04	0.05
2.5	0.03	0.04	0.05	0	0.01	0.01
8.5	0.05	0.05	0.05	0.02	0.07	0.06
14.5	0.02	0.08	0.09	0.05	0.04	0.03
22.5	0.09	0.06	0.07	0.09	0.09	0.07
26.5	0.03	0.04	0.9	0.6	0.06	0.09
32.5	0.1	0.09	0.06	1.2	0.06	0.5
38.5	0.3	0.08	0.4	2.1	0.3	1.1
46.5	0.4	0.07	1	1.8	0.5	3.1
58.5	0.3	0.06	0.8	1	1.1	7
70.5	0.2	0.1	0.7	1.4	2.5	6.2
82.5	0.2	0.15	0.6	1.4	2.2	5.8
94.5	0.3	0.1	0.8	1.8	2.7	5.8
106.5	0.3	0.15	1.5	3	2.8	6
118.5	0.8	0.2	2.1	2.5	4.4	8.12
130.5	0.6	0.4	2.4	3.2	5.8	12.2
142.5	0.5	0.8	2.7	3.5	5.8	10.4
166.5	0.5	0.8	2.9	6.2	5.8	
190.5	0.7	0.9		4.2	5.8	
214.5	0.9	1		5.7	6.3	
238.5	1	1.9		6	6.6	

Effluent pH

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	5.95	4.87	6.81	5.01	4.68	4.74
2.5	4.86	4.68	5.25	4.9	6.08	5.47
8.5	4.73	5.17	4.78	5.69	5.88	5.08
14.5	4.51	5.48	6.62	5.33	5.64	5.55
22.5	4.04	6	6.14	5.52	6.11	6.22
26.5	3.83	5.72	6	5.29	5.88	6.01
32.5	3.92	5.49	6.09	5.02	5.27	6.15
38.5	3.77	5.44	6.15	4.12	5.24	6.35
46.5	3.33	4.4	6.45	3.63	4.57	6.3
58.5	3.51	4.27	6.7	3.61	4.61	6.61
70.5	3.57	4.2	7.33	3.44	4.33	6.99
82.5	3.13	3.69	7.21	3.08	4.11	6.79
94.5	3.33	4.05	8.14	3.25	4.67	8.06
106.5	3.29	3.98	9.05	3.07	4.4	8.77
118.5	3.33	4.1	9.2	3.26	4.24	9.05
130.5	2.95	5.66	9.18	2.98	4.98	9.16
142.5	3.4	5.73	9.19	3.18	4.41	9.12
166.5	3.16	4.05	9.3	3.06	3.93	
190.5	3.43	4.28		3.24	4.24	
214.5	3.3	5.04		3.31	4.04	
238.5	3.2	6.13		3.19	4.04	

Effluent Temperature (^{0}C)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	25.1	25.3	24.9	25	24.8	25.1
2.5	24.7	24.9	24.8	24.8	24.8	24.6
8.5	24.9	25	25	24.8	24.7	24.7
14.5	24.1	24.2	24.3	24.2	24.1	24.1
22.5	23.3	23.2	23.2	23.2	23.1	22.9
26.5	23.5	23.6	23.4	23.5	23.8	24.1
32.5	25.2	25.4	25.6	25.7	25.7	25.8
38.5	25.4	25.3	25.2	25.2	24.9	24.9
46.5	23.3	23.4	23.7	23.7	23.8	23.9
58.5	25.5	25.7	25.7	25.5	25.5	25.5
70.5	25	25.4	25.2	25.3	25.4	25.5
82.5	27.1	27.2	27.2	27.4	27.4	27.5
94.5	29.2	30.1	29.6	30	29.7	30.2
106.5	26.8	26.9	26.7	26.7	26.8	26.8
118.5	25	25.1	25.7	25.3	25.7	25.9
130.5	23.4	23.5	23.8	23.6	23.6	23.4
142.5	24.4	24.5	24.6	24.5	24.6	24.6
166.5	24.7	24.9	24.9	25	25.2	
190.5	24.4	24.3		24.3	24.4	
214.5	21.1	21.1		21.1	21.1	
238.5	23.5	23.6		23.4	25.5	

Effluent Soluble Aluminum (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	1.15	1.75	2.85	3.3	1.5	1.35
10	1.15	1.15	0.35	0.6	0.9	0.6
24	3.25	0.95	0.5	0.35	0	0.5
34	4.8	0.6	0.3	0.25	0.55	0.6
34	11.85	0.25	0.6	8.3	0.4	0.75
48	11.95	2.2	3.2	15.95	1.2	1.85
72	11.65	1.1	9.35	14.6	0.9	7.15
96	8.45	1.3	46	9.7	1.3	7.15
120	8.15	0.6	50	9.15	0.7	41.9
144	8.45	0.65	53.6	8.4	0.65	45
192	8.5	0.45		5.95	1.4	

Effluent BOD$_5$ (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	9.6	11.4	14.7	54	11.1	83.4
10	6.9	7.2	11.4	9.3	4.5	2.4
24	4.8	2.4	3.6	10.5	31.5	6.6
34	6.6	2.1	2.1	9.3	2.4	2.1
34	33	28.5	38.4	40.8	30.6	25.2
48	17.7	4.2	2.7	3.9	3.9	4.2
72	51.9	48	54.9	48.9	47.7	46.8
96	9.9	21.9	5.1	0.9	0.9	28.5
120	15.9	6.9	28.2	18.9	18.3	20.1
144	20.7	1.2	1.5	0.6	0.6	
192	0.9	0.6		1.2	0.6	

Operating Condition for Experiments (including duplicate) Conducted on Particle Size

Porosity

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Blank (B) (g)	68.6	68.5	68.3	69.1	68.6	68.6
B+Dry samples (g)	154.4	154.3	153.9	152.1	152	154.4
B+Wet samples (g)	208.7	212.3	212.5	209.9	211.4	208.7
Porosity	0.543	0.58	0.586	0.578	0.594	0.543

Flow rate (mL/min)

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Beginning	2.3	2.2	2.35	1.9	2.1	2.3
End	2.3	2.2	2.35	1.9	2.1	2.3
Average	2.3	2.2	2.35	1.9	2.1	2.3

Operating variables

	Column1	Column2	Column3	Column4	Column5	Column6
pH	5.41	5.41	5.41	5.41	5.41	5.41
Initial P (mg/L)	2.5	2.5	2.5	2.5	2.5	2.5
Particle size (mm)	1.20	0.98	0.73	1.20	0.98	0.73
Porosity	0.543	0.58	0.586	0.578	0.594	0.543
Flowrate (mL/min)	2.3	2.2	2.35	1.9	2.1	2.3

Effluent Phosphorus Concentration (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	0.01	0.01	0.02	0	0	0
4	0.06	0.05	0.03	0	0.01	0
8	0.02	0.06	0.02	0.02	0.04	0
12	0.03	0.06	0.01	0.02	0.06	0
16	0.03	0.07	0.02	0.04	0.07	0
24	0.09	0.02	0.03	0.05	0.05	0
28	0.01	0.08	0.04	0.03	0.08	0
32	0.04	0.01	0.05	0.02	0.07	0
36	0.06	0.04	0.05	0.03	0.09	0
40	0.02	0.07	0.05	0.04	0.07	0
48	0.09	0.08	0.01	0.07	0.11	0.02
54	0.09	0.11	0.07	0.09	0.15	0.03
60	0.08	0.07	0.09	0.13	0.19	0.01
72	0.13	0.15	0.01	0.23	0.26	0.05
80	0.31	0.26	0.09	0.34	0.38	0.09
84.5	0.42	0.36	0.08	0.52	0.58	0.13
96	0.62	0.51	0.15	0.73	0.78	0.23
103	0.75	0.87	0.19	0.87	0.94	0.1
109	0.91	0.95	0.23	0.94	0.9	0.43
120	1.6	1.13	0.34	1.3	1.2	0.75
133.5	1.7	1.35	0.49	1.4	1.35	0.85
144	1.7	1.5	0.6	1.5	1.5	1.2
168	1.9	1.7	1.05	1.6	1.5	0.4
192	1.9	1.2	1	1.6	1.1	1.5
216		1.2	1.4	1.7	1.8	2.4
240		1.1	1.2			
288		1.8				

Effluent pH

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	4.52	4.72	4.41	4.52	4.4	4.56
4	3.89	3.99	4.43	3.74	3.61	3.68
8	3.83	3.81	3.93	3.7	3.71	3.86
12	4.07	4.17	4.1	3.78	3.75	3.79
16	4.00	4.02	3.92	3.77	3.8	3.78
24	3.82	3.92	3.96	3.95	4.01	4.13
28	3.81	3.85	3.83	3.93	3.84	3.91
32	3.72	3.82	3.64	3.89	3.84	3.95
36	3.83	3.93	3.84	3.87	3.82	3.95
40	3.88	3.98	3.77	3.95	3.87	3.99
48	4.03	4.09	3.64	3.7	3.67	3.79
54	4.05	4.01	4.06	4.08	4	4.13
60	4.06	4.12	4.15	4.11	4	4.07
72	4.12	4.42	4.12	4.28	4.21	4.53
80	4.14	4.4	4.11	4.36	4.11	4.48
84.5	4.28	4.23	4.15	4.17	4.54	4.51
96	4.42	4.32	4.29	4.62	4.29	4.62
103	4.56	4.36	4.25	4.4	4.72	4.21
109	4.69	4.78	4.59	4.48	4.2	4.77
120	4.73	4.93	4.79	4.83	4.46	4.89
133.5	5.03	5.13	4.98	4.83	4.53	4.93
144	5.21	5.26	5.02	4.78	4.58	4.9
168	5.11	5.15	4.84	4.81	4.62	4.58
192	5.21	5.31	4.89	4.89	4.89	5.16
216	5.32	5.42	5.15	5.12	5.54	5.43
240	5.41	5.42	5.41			
288	5.59	5.49				

Effluent Temperature (^{0}C)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	22.1	22.3	22.5	22.9	23.3	24.2
4	23.1	23.3	23.3	23.9	24	24.4
8	24.2	24.3	24.3	24.4	24.5	24.5
12	23.4	23.5	23.8	23.3	23.9	23.4
16	23.1	23.2	23.2	22.8	22.7	22.5
24	23.5	21.6	21.7	21.8	21.7	21.7
28	23.5	23.6	24.5	24.8	24.7	25
32	24.5	24.4	25	25.1	25	25.1
36	23.2	23.3	23.7	23.7	23.6	23.6
40	23.3	23.4	23.8	23.9	23.7	23.6
48	22.7	22.8	22.6	22.8	22.6	22.6
54	24.4	24.5	24.6	25.5	25.4	25.5
60	24.5	24.6	24.7	24.6	24.5	24.4
72	23.1	23	24	24.8	25.2	24.2
80	24.5	24.4	24.9	25.2	25.3	25.5
84.5	23.8	23.9	23.9	23.8	23.6	23.7
96	21.9	21.8	22	22.2	22.1	22.7
103	23.6	23.7	23.9	23.8	23.6	24.3
109	24.3	24.2	24.4	24.8	24.2	24.1
120	22.1	22	22	22.3	22.3	22.3
133.5	23.8	23.7	23.7	23.7	23.5	23.3
144	22.1	22	22.2	22.2	22.2	22.2
168	23.7	23.7	23.8	23.9	23.9	23.9
192	22.4	22.5	22.5	22.4	22.7	22.5
216		23.3	23.3	23.2	23.3	23.4
240		22.3	22.5			
288		23.3				

Effluent Soluble Aluminum (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	2.5	3.45	5.44	2.1	4.65	4.75
8	3.3	2.3	6.10	4.2	3.4	6
16	2.8	1.65	5.57	2.6	1.85	4.45
24	1.9	1.35	3.57	1.7	1.55	2.75
32	1.65	1.02	2.98	1.55	1.45	2.3
40	1.29	0.93	2.54	1.3	1.3	2
48	1.18	1.01	1.9	1.2	1.15	1
60	0.95	1.05	1.54	0.85	1.35	1.35
72	0.56	0.65	0.18	0.085	0.065	0.075
96	0.15	0.17	0.098	0.185	0.175	0.135
120	0.05	0.11	0.087	0.155	0.16	0.08
168	0.04	0.05	0.075	0.115	0.11	0.115

Effluent BOD$_5$ (mg/L)

Time (hours)	Column1	Column2	Column3	Column4	Column5	Column6
0	8.3	7.5	3.5	12.3	15.6	2.4
8	10.3	14.4	5.4	15.3	18.9	5.7
16	3.6	1.8	3.1	0.6	0.6	3.9
24	1.2	6.9	0.9	4.2	2.7	3
32	10.7	27.7	9.1	11.7	12.9	8.1
40	11.2	26	1.7	13.2	0.9	0.6
48	13.9	11.4	8.5	9.9	4.5	13.5
60	9.9	28.2	13.2	12.9	26.1	20.7
72	11	14.1	4.8	18	24.3	1.2
96	5.2	27.3	27.9	1.2	13.8	20.7
120	8.4	14.7	15.3	11.4	13.2	8.7
168	11.6	29.8	38.7	15.6	15	45.3

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APPENDIX C: EXPERIMENTAL TRIAL OF CHAPTER 8

Estimation of specific surface area (oven dried alum sludge)

	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
Can (g)	2.21	2.23	2.19	2.19	2.2	2.23
Can + Sludge (g)	2.89	2.88	2.92	2.88	2.89	2.87
Can + Dry Sludge (g)	2.82	2.81	2.85	2.8	2.81	2.78
Can + Dry Sludge + Ethylin glycol (g)	3.49	3.25	3.62	3.25	3.33	3.27
Ethylin glycol (g), Wa	0.67	0.44	0.77	0.45	0.52	0.49
Dried Sludge (g), Ws	0.61	0.58	0.66	0.61	0.61	0.55
Specific surface area (m^2/g)	3840.42	2652.52	4079.25	2579.39	2980.63	3115.07
Average (m^2/g)	3207.88					
Standard deviation (m^2/g)	620.18					

Estimation of specific surface area (air dried alum sludge)

	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6
Can (g)	2.174	2.1329	2.105	2.111	2.0981	2.1225
Can + Dry Sludge (g)	2.836	2.833	2.782	2.811	2.788	2.800
Can + Dry Sludge + Ethylin glycol (g)	2.862	2.857	2.818	2.826	2.802	2.829
Ethylin glycol (g), Wa	0.662	0.700	0.677	0.700	0.690	0.677
Dried Sludge (g), Ws	0.026	0.023	0.035	0.014	0.013	0.029
Specific surface area (m^2/g)	137.262	117.747	185.330	74.3936	70.4266	152.739
Average (m^2/g)	122.9835					
Standard deviation (m^2/g)	45.00471					

APPENDIX D: ANOVA TABLES FOR TESTS ON pH AND PARTICLE SIZE

Particle size: 1180 μm

Initial phosphorus concentration: 2.5 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.7419	6.68547	338.56	0.000
pH	0.1354	0.06769	3.43	0.059
Interaction	0.1126	0.01407	0.71	0.678
Residual	0.2962	0.01975	—	—

Particle size: 1180 μm

Initial phosphorus concentration: 10 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	469.247	117.312	317.20	0.000
pH	8.990	4.495	12.15	0.001
Interaction	6.332	0.791	2.14	0.097
Residual	5.547	0.370	—	—

Particle size: 425 μm

Initial phosphorus concentration: 2.5 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.8919	6.72298	1239.64	0.000
pH	0.0137	0.00687	1.27	0.310
Interaction	0.0251	0.00313	0.58	0.781
Residual	0.0813	0.00542	—	—

Particle size: 425 μm

Initial phosphorus concentration: 10 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	487.799	121.950	2423.64	0.000
pH	0.241	0.120	2.39	0.125
Interaction	1.964	0.245	4.88	0.004
Residual	0.755	0.050	—	—

Particle size: 250 μm

Initial phosphorus concentration: 2.5 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.1226	6.53066	5678.83	0.000
pH	0.0009	0.00043	0.37	0.694
Interaction	0.0123	0.00154	1.34	0.297
Residual	0.0172	0.00115	—	—

Particle size: 250 μm

Initial phosphorus concentration: 10 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	571.664	142.916	950.13	0.000
pH	0.224	0.112	0.74	0.492
Interaction	1.325	0.166	1.10	0.414
Residual	2.256	0.150	—	—

pH: 3

Initial phosphorus concentration: 2.5 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.0997	6.52492	567.38	0.000
Particle size (μm)	0.1685	0.08424	7.33	0.006
Interaction	0.0303	0.00378	0.33	0.942
Residual	0.1725	0.01150	—	—

pH: 3

Initial phosphorus concentration: 10 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	471.496	117.874	4464.92	0.000
Particle size (μm)	0.175	0.087	3.31	0.065
Interaction	0.789	0.099	3.73	0.013
Residual	0.396	0.026	—	—

pH: 5

Initial phosphorus concentration: 2.5 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.7700	6.69251	3340.69	0.000
Particle size (μm)	0.0130	0.00650	3.25	0.067
Interaction	0.0098	0.00122	0.61	0.756
Residual	0.0301	0.00200	—	—

pH: 5

Initial phosphorus concentration: 10 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	536.207	134.052	1813.06	0.000
Particle size (μm)	0.128	0.064	0.86	0.441
Interaction	0.991	0.124	1.68	0.185
Residual	1.109	0.074	—	—

pH: 7

Initial phosphorus concentration: 2.5 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	26.8033	6.70082	522.82	0.000
Particle size (μm)	0.1810	0.09050	7.06	0.007
Interaction	0.1933	0.02416	1.89	0.138
Residual	0.1922	0.01282	—	—

pH: 7

Initial phosphorus concentration: 10 mg/L

Source	Sum of Square	Mean Square	F value	p value
Alum sludge (g/L)	517.995	129.499	275.40	0.000
Particle size (μm)	7.401	3.701	7.87	0.005
Interaction	10.853	1.357	2.89	0.037
Residual	7.053	0.470	—	—