THESIS

SIMULTANEOUS PHOSPHORUS AND NITROGEN REMOVAL USING

ALUMINUM BASED WATER TREATMENT RESIDUAL

Submitted by

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ABSTRACT

SIMULTANEOUS PHOSPHORUS AND NITROGEN REMOVAL USING

ALUMINUM BASED WATER TREATMENT RESIDUAL

In this study, an aluminum-based water treatment residual (Al-WTR) from a local

water treatment facility was investigated for its capacity for phosphorus (P) and nitrogen

(N) removal in wastewater.

Characterization results indicated that Al-WTR had a high content of amorphous

aluminum hydroxide, which is able to bond phosphorus in solution mainly via ligand

exchange. Also, Al-WTR was found to be rich in bio-available carbon, which can

facilitate biological denitrification for N removal.

Batch equilibrium tests analyzed the P sorption parameters according to Langmuir

and Freundlich isotherms. The results of the maximum sorption capacity were 4.498,

3.258 and 2.038 g/kg at pH values of 4, 7, and 9 respectively, indicating that P sorption

was favored at lower pH conditions. However, the sorption capacity results may not

reflect that in continuous-flow conditions. Al-WTR was shown to be a more effective

sorbent for orthophosphate phosphorus (ortho-P) than total phosphorus (TP), but still had

promising removals (greater than 90%) to both. Simultaneous P and N removal in wastewater was tested in column experiments in a continuous-flow mode. 95.9% removal of ortho-P and 90.0 % removal were achieved. Also, NO_3^- removal was highly efficient (99.6%).

In sum, using Al-WTR as a P and N mitigation agent is a feasible and sustainable technology, and could be applied in P and N control practices in point-sources and non-point sources.

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Chapter 1   INTRODUCTION

Nitrogen (N) and phosphorus (P) are two essential nutrients for all forms of life on earth. On one hand, they are of crucial importance to modern agriculture and industrial development; on the other hand, production of N and P from anthropogenic activities can result in environmental issues.

Eutrophication is an important environmental concern associated with P and N in surface water bodies. It is generally defined as a status of surface water characterized with nutrient enrichment that induces blooms of algae and aquatic plants, decrease of dissolved oxygen, and degradation of water quality (Yeoman et al., 1988). Although eutrophication was found to proceed slowly in natural conditions and the causes of eutrophication are complex, excessive phosphorus (P) and nitrogen (N) inputs as a result of human activities can accelerate the process greatly (Yeoman et al., 1988). The health risk to human of N pollution is another concern. N is a dynamic and mobile element in the natural environment. In the ammonia or ammonium (NH_3/NH_4^+) form, it is highly toxic to aquatic animals (Thurston et al., 1981). Nitrate nitrogen ($NO_3\text{-}N$), which is very

soluble, can pollute surface and ground water via runoff and infiltration respectively. Excessive concentration of NO_3^- intake by human body through drinking water or food can cause methemoglobinemia ("blue baby syndrome") or carcinogenic effects (Pierzynski et al., 2005). As a result, the management of P and N in natural waters has long been of importance from environmental, health, and economic perspectives.

The currently prevailing methods for nitrogen and phosphorus removal in wastewater treatment plants (WWTPs) include chemical precipitation and biological processes based on activated sludge in secondary or tertiary treatments. However, these nutrient removal processes, because of the requirements of their costs, operation and maintenance, are usually not available for small-scale and decentralized treatment systems, such as WWTPs in rural areas or small towns, septic ponds and waste lagoons, which are still being widely used in this country and the world. Failures of these treatment systems to reduce nutrient contents could increase anthropogenic N and P discharged to natural waters. Therefore, the development of low-cost and efficient technologies for nutrient control in small-scale and dispersed treatment systems can have an important impact on water quality.

The use of fixed-bed filters with reactive or sorptive media for nutrient removal has been considered an effective and economic treatment alternative for nutrient control in water or wastewater environments. The filter media could be naturally occurring (e.g.,

sand, oyster shell), engineered (e.g., light weight aggregates), or industrial byproduct (e.g., slag, fly ash) (Westholm, 2006; Vohla et al., 2009; Chang et al., 2010). Chang et al. (2010) identified the nutrient removal mechanisms of these "filter media" to be both physicochemical processes, such as adsorption, absorption, ion exchange, and precipitation, and microbiological processes, such as nitrification and denitrification. This study focused on the use of drinking water treatment residual (WTR), which is a byproduct of the drinking water treatment industry, as the filter media for P and N removal and its possible applications in small or dispersed wastewater treatment facilities and waste lagoons.

In typical drinking water treatment practice, WTRs are generated from the coagulation/separation processes, in which Fe or Al salts, usually together with polyelectrolytes, are added to raw water for the removal of colloids, color, suspended solids and common contaminants. The sediments are settled, separated and concentrated in dry basins finally to form WTRs. Depending on the raw water quality and treatment processes, the compositions and properties of WTRs vary widely. Generally, these materials have a high content of metal (hydr)oxides and organic carbon. Because of the high production of WTRs over the world, treatment and disposal induces cost and technical problems. The common disposal options of WTR include directly discharging to surface waters, discharge to wastewater treatment plants, landfilling, and land

application (U.S. EPA et al., 1996). In the state of Colorado, regulations require WTRs to be tested for hazardous and radioactive contaminants before disposal or reuse. However, generally, WTRs are not considered hazardous wastes (U.S. EPA et al., 1996).

The beneficial uses of WTRs for nutrient reduction in wastewater have been widely investigated (Makris and O'Connor, 2007; Babatunde and Zhao, 2007). Aluminum and ferric hydroxides, especially in amorphous form, have been observed to adsorb phosphorus from solutions via ligand exchange. WTRs are characterized to have high contents of aluminum or ferric hydroxides, depending on the kind of metal salt added in the water treatment process, and therefore expected to be an effective sorbent of phosphorus. P sorption mechanisms on WTR include ion exchange, surface precipitation, and ligand exchange, of which ligand exchange is considered dominant (Yang et al., 2006). Also, two phases of the sorption for P have been identified, that is, an initial fast reaction (typically within 24 hours) for P being bonded to the surface of the sorbent, and a slow reaction (1 week or longer) for the movement of sorbed P to the inner part of the sorbent particles (Pierzynski et al., 2005).

On the other side, the N reduction capacity of WTRs has not been investigated as much as for P. However, the nature of WTRs makes it possible to act as a biofilm carrier for denitrification. Bearing a high content of an active carbon (C) source, the WTR surface can facilitate the biological denitrification process and have the potential to

achieve P and N removal simultaneously under proper conditions. Also, the use of WTRs not only provides a low-cost technological solution for nutrient control, but also an effective residuals management option for water treatment facilities.

The purpose of this research project was to investigate the efficacy of Al-WTR as a filter medium for removing P and N from domestic wastewater. For this purpose, bench-scale experiments were conducted including Al-WTR characterization, batch tests for P sorption behavior in equilibrium conditions and column tests for P and N removal under continuous flow. The objectives of this study include:

(1) Characterizing the Al-WTR to examine the composition and properties of the material.

(2) Investigating the processes of phosphorus-sorption and denitrification in the Al-WTR, as two essential removal mechanisms.

(3) Discussing the potential applications for the Al-WTR as a media material in fixed-bed filters to control P and N from entering watersheds.

Chapter 2   LITERATURE REVIEW

2.1 Phosphorus and nitrogen and the environmental impacts

2.1.1 Phosphorus in the environment

Phosphorus in the natural water environment occurs almost solely in the ortho-phosphate form, that is, pentavalent state and coordinated to oxygen atoms or hydroxyl groups (APHA, 1992; Jenkins et al., 1971). Although P is not redox active, it can exist in various phosphate species, which are classified as orthophosphates, condensed phosphates, and organic phosphates (Jenkins et al., 1971). In wastewater, typical levels of P in different forms were estimated by Jenkins et al. (1971) as orthophosphate 5 mg P/L (50%), tripolyphosphate 3 mg P/L (30%), pyrophosphate 1 mg P/L (10%), and organic phosphates 1 mg P/L(10%). On the one hand, orthophosphate is of significant concern because it is not only the most abundant form of P in water and wastewater, but also is the form that can be immediately utilized by organisms (APHA, 1992; Jenkins et al., 1971). On the other hand, TP is regulated and usually is of most concern. This is because even though not immediately available for organisms, other species of P are eventually

available and therefore of concern. Also, P in aquatic environments can be divided into dissolved phosphates and particulate phosphates. The former refer to the dissolved phosphate ions in water and the latter are those attached to suspended solid particles.

Analytical procedures have been established to characterize different P species. Filtration through a 0.45-µm membrane filter separates dissolved from suspended forms of phosphorus. Phosphates that respond to "colorimetric tests without preliminary hydrolysis or oxidative digestion" of the sample are termed reactive phosphorus (RP), which is often used to approximately represent orthophosphates (APHA, 1992). Generally, other forms of P are first hydrolyzed or digested and then measured as orthophosphates by colorimetric methods.
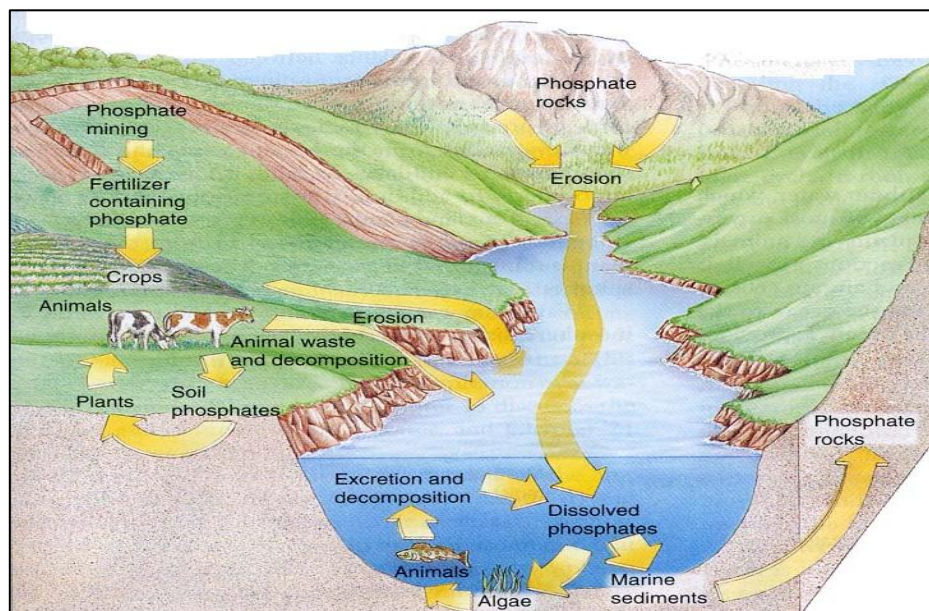
Figure 2-1 Phosphorus cycle
(http://vincejtremante.tripod.com/cycles/phosphours.htm)

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Figure 2-1 illustrates the P cycle in nature. In aquatic environments, P is not redox active and primarily in the forms of phosphates (APHA, 1992). P transport from land to ocean is considered an irreversible process because of the long geological duration of the regeneration of phosphate minerals (Carpenter and Bennett, 2011). Presently, the human demand of P, as an important resource for agriculture and industry, is mostly dependent on phosphorus mining. However, it has been reported with the current rate of P mining, global scarcity of P could be a problem within several decades (Carpenter and Bennett, 2011). As a result, the development of P recovery technologies is generating increasing interest.

2.1.2 Nitrogen in the environment

Nitrogen is a very dynamic element, capable of being transformed biochemically or chemically through a series of processes conceptually summarized as the nitrogen cycle (Figure 2-2).

Most transformations involve the oxidation or reduction of the N atom through both biological and chemical processes. The oxidation states of N in nature range from +5 in the nitrate anion to -3 for the ammonium cation (Pierzynski et al., 2005). The natural sources of N in water include biological N fixation of atmospheric N_2 by aquatic plants, decomposition, atmospheric deposition, and weathering (Pierzynski et al., 2005). However, anthropogenic sources have played an important role in the total amount of the

N pool in aquatic environments. Generally, N attribution from human activity is classified into point sources and non-point sources. Point sources refer to wastewater from municipalities and industry treated in wastewater treatment plants (WWTPs), which is discharged to a water body. For the non-point sources such as fertilizer applied agriculture land and livestock facilities, N can be transferred either by runoff directly into surface water, causing eutrophication, or via leaching into groundwater, threatening the ground water quality and eventually entering surface water bodies. Also, N leaching from septic tanks and waste lagoons can be a concern (Pidwirny, 2006). Actually, nonpoint source pollution has become more important as a contributor to nutrient pollution globally. Research by Pierzynski et al. (2005) in 15 major watersheds in the U.S. found nonpoint N pollution was much larger than that from point sources.
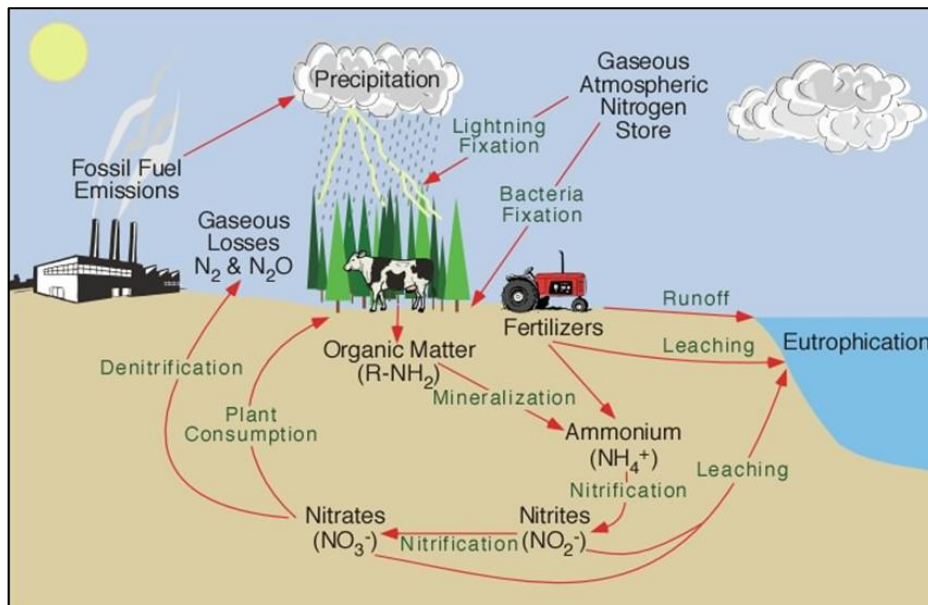
Figure 2-2 Nitrogen cycle

2.1.3 Environmental impacts of nitrogen and phosphorus in waters

Eutrophication can be defined as "the enrichment of waters by nutrients and the consequent deterioration of quality due to the luxuriant growth of plant life, and its repercussions on the ecological balance of the waters affected" (Yeoman et al., 1988). When eutrophication takes place, the high concentrations of nutrients in water bodies promote the growth of algae and aquatic plants. The consequential bloom of algae and aquatic plants can eliminate the dissolved oxygen in the water body to create hypoxia (DO level < 2 mg/L). Its consequences often include water quality degradation, death of aquatic life, odor and taste problems, and poison effects generated by algae to fish and even livestock (Yeoman et al., 1988). The enormous damage to ecological, health and economic values has become a serious issue in recent decades.

Although the causes of eutrophication can be complicated, the enrichment of nutrients in water bodies is known to be the most important contributor. N and P are the two most important nutrients for their role in eutrophication (Pierzynski et al., 2005). Yeoman et al. (1988) found eutrophication proceeds slowly in the natural ageing of lakes, but could be accelerated by the input of phosphorus. The Redfield ratio (or Redfield stoichiometry) reveals the molecular ratio of carbon, nitrogen and phosphorus in phytoplankton as C:N:P = 106:16:1 (Redfield, 1934). Since carbon in natural water is

often considered as limitless because of the source of carbon dioxide in the atmosphere, algae growth could be limited by the deficiency of either N or P, and the limiting one is considered to be most important for eutrophication control. For example, water bodies with a P concentration lower than the limiting level will be more sensitive to external inputs of P than N. Redfield ratio offered a principle to determine which nutrient is the limiting one. When N:P > 16:1, P is most likely the limiting nutrient; if in the opposite, N is of greater concern. Generally, the limiting nutrient in most fresh waters is phosphorus, but in most sea waters is nitrogen. This is mainly because the P supply in sea waters is abundant while P levels in fresh waters are often low (Blomqvist et al., 2004). Pierzynski et al. (2005) presented an estimation of the eutrophication threshold for P (~20 to 100 μg P/L) and for N (~500 to 1000 μg N/L) in most aquatic systems. Actually, it has been reported that even 10 μg/L (ppb) of total P concentration can cause problems (Correll, 1998). As a result, P is usually considered as the indicator of the trophic status in fresh waters.

Other than eutrophication, or algae blooms, the excess input of nutrients may also cause the harmful algae bloom (HAB), which is defined as "an algal bloom that causes negative impacts to other organisms via production of natural toxins, mechanical damage to other organisms, or by other means" (CDC, 2004). While most species of algae are not harmful or toxic, some HAB-causing species can be dangerous to other lives by releasing

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natural toxins (CDC, 2004). For example, the Cyanobacteria, also known as blue-green algae, have been reported as tainting fresh water and being toxic to humans, pets and other animals (CDC, 2004). The HABs in marine areas are often associated to the "red tides", of which the consequences include lethal toxins to marine animals. HABs have also been a global problem. It has been reported to be associated with environmental problems in over 45 countries worldwide and in at least 27 U.S. States (Graham, 2007).

The concerns for N also include deleterious effects on humans and animals. N in the ammonia (NH_3) form is highly toxic to fish and other aquatic life (Thurston et al., 1981) and as a result, NH_3/NH_4^+ has stringent permit limits for wastewater treatment discharge. Nitrate (NO_3^-) in drinking water is also a common concern. Excessive intake of NO_3^- by humans via drinking water or food can induce methemoglobinemia ("blue baby syndrome") or carcinogenic effects (Pierzynski et al., 2005).

2.2 Phosphorus and nitrogen removal technologies

2.2.1 Overview of phosphorus removal technologies

Water Environment Federation (WEF) (1998) summarized different approaches available for P removal as shown in Figure 2-3. Phosphorus is typically removed in WWTPs by two processes: chemical precipitation and/or biological removal. For chemical precipitation, phosphorus is removed by conversion to chemical precipitates with addition of metal salts or lime. Most organic and inorganic forms of phosphorus are

readily removed by precipitation with the use of alum, ferric salts, or lime (USACE, 2001). Biological P removal is achieved by incorporating P into the biological cell mass. In enhanced biological P removal processes, the biomass is able to accumulate phosphorus to levels that far exceed the nutritional requirements. The biological treatment of P is often combined with N removal and called Biological Nutrient Removal (BNR) by introducing anaerobic and/or anoxic stages in the activated sludge process.
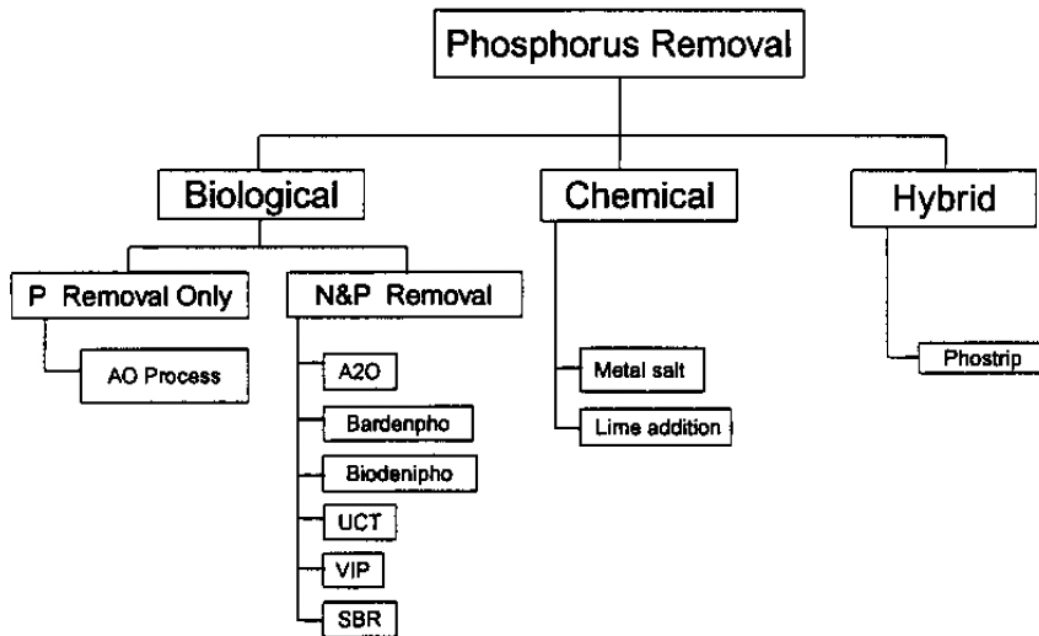
Figure 2-3 Summary of phosphorus removal technologies (WEF, 1998)

In addition, some novel technologies have also been investigated for their potential to remove phosphorus from wastewater, including ion exchange, struvite crystallization, magnetic attraction and sorption. Sorption is the focus of this study. Although the approach is still mostly investigated at laboratory scale, the potential advantages include

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no reagent requirements, no additional sludge generation, easy operation and low cost materials in wastewater practices.

2.2.2 Mechanism of phosphorus sorption

Sorption is a general term of adsorption and absorption. Absorption is defined as the incorporation of a substance in one state into another of a different state, and adsorption refers to the physical adherence or bonding of ions and molecules onto the surface of another phase (Benjamin, 2002). It is often impossible to distinguish the two mechanisms in the process that aqueous phosphorus is taken up or retained by solid media (e.g. soils). Ligand exchange of phosphate ions and metal hydroxides on media surfaces is believed to be the predominant mechanism for the sorption of phosphorus (Yang et al., 2006). When contacting with aqueous solutions, the metal (hydr)oxides on the surface of the sorbent material become hydrated or hydroxylated, serving as the binding sites. Phosphate anions can be exchanged with the hydroxyl ions on the solid surface to form surface complexes, thus being immobilized. (Guan, 2005). For orthophosphates the ligand exchange reaction can be described as shown in Equation 2-1 (Rajan et al., 1974).

$$aMOH_{(s)} + H_bPO_{4(aq)}^{(b-3)} + cH_{(aq)}^+ \leftrightarrow M_aH_cPO_{4(s)} + bH_2O_{(l)} + (a-b)OH_{(aq)}^- \quad (2\text{-}1)$$
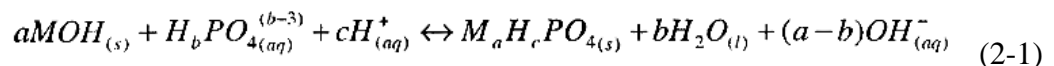
Where M stands for a metal ion (usually Al of Fe), and b ($\leqslant$3) refers to the degree of protonation of an orthophosphate ion.

Figure 2-4 shows the possible forms of phosphorus surface complexes.
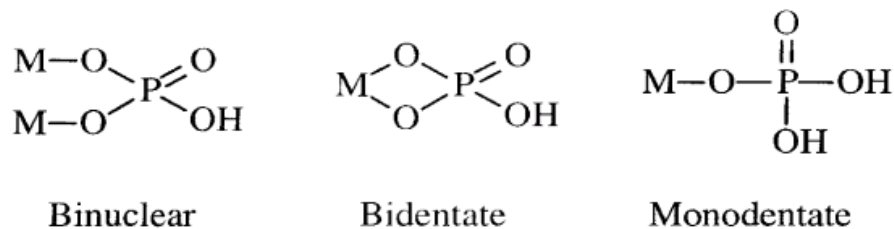
Figure 2-4 Forms of surface complexes

P sorption is pH dependent because the surface hydroxyl groups vary with pH. The

process is described as Equation 2-2 and 2-3 (Parfitt et al., 1975).

$$MOH_2^+ \xrightarrow{+OH^-} MOH + H_2O \qquad (2\text{-}2)$$

$$MOH \xrightarrow{+OH^-} MO^- + H_2O \qquad (2\text{-}3)$$
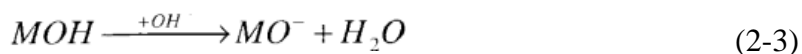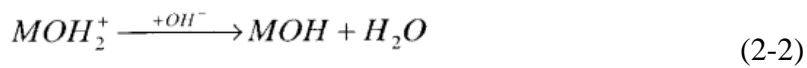
Depending on the solution pH, an excess or a deficiency in protons may be present at

the interface, thus leading to positively or negatively charged surfaces.

As a result, the sorption reaches a maximum at low pH and then decreases with

increasing pH, owing to the proton release from the ligand exchange reactions. Therefore,

pH is an important influencing factor for the design of P sorption processes.

P sorption is considered as a kinetically biphasic process (Pierzynski et al., 2005),

that is, it has a rapid initial reaction, typically 1 day or less, and a slow later reaction that

can last for weeks or longer. The rapid initial phase represents anion exchange and ligand

exchange on mineral edges or by amorphous oxides and carbonates. The slow reaction

involves precipitation or polymerization on mineral surfaces or diffusion of adsorbed P

into the interior of solid phases (Pierzynski et al., 2005). This biphasic reaction

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mechanism is important for understanding how P sorbents saturate over time.

2.2.3 Overview of nitrogen removal technologies

The most prevalent forms of nitrogen in wastewaters are organic, ammonium and nitrate nitrogen (Sedlak et al., 1991). However, only less than 1% of N exists in the oxidized form of nitrate in raw wastewater. Typically organic (60%) and ammonium (40%) forms of N are the dominating forms in domestic water (Sedlak et al., 1991). Depending upon the local circumstances, removal of all forms of nitrogen or just ammonium may be required. N removal processes are summarized in Figure 2-4.
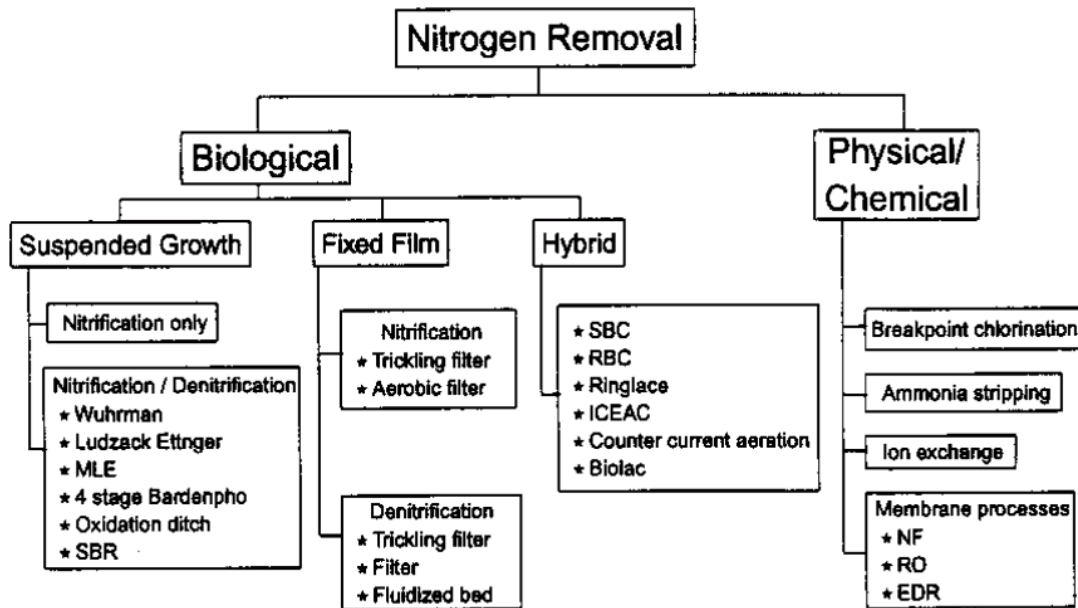
Figure 2-5 Summary of nitrogen removal technologies (WEF, 1998)

Despite other options, biological treatment processes for N removal are the dominant method for being efficient, economical and practical (USACE, 2001). Nitrification and denitrification are two essential processes for biological N removal. Nitrification is the

biological oxidation of ammonia (NH_3)/ammonium (NH_4^+) to nitrate with nitrite as an intermediate. Nitrification depends on the presence of both nitrifying organisms (autotrophic) and oxygen. Denitrification is the biological conversion of nitrate-nitrogen to more reduced forms such as N_2, N_2O and NO. The requirements for denitrification include the denitrifying organisms (autotrophic or heterotrophic), nitrate ions, carbon source and the absence of oxygen (Firestone, 1982).

Since nitrification just transforms the oxidation status and the forms of nitrogen, it doesn't really removal nitrogen from water and may be applied without denitrification for the circumstances that only ammonia removal is required. On the other side, denitrification utilizes the nitrate generated by nitrification and reduces the N to an inert gas (N_2) that volatilizes out of the water. As a result, combined nitrification and denitrification systems are often used to achieve total N removal. The systems have either two basins for nitrification and denitrification separately, or one basin with two stages shifting between anoxic and aerobic conditions so that the nitrification and denitrification can take place consecutively.

2.2.4 Mechanism of nitrification and denitrification

Nitrification involves the conversion of ammonium to nitrite, and finally to nitrate. The conversion to nitrite is catalyzed by Nitrosomonas sp., and the conversion to nitrate by Nitrobacter sp. In practice, the kinetics of the overall process are limited by

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Nitrosomonas sp., and nitrite is rapidly converted to nitrate by Nitrobacter sp.; therefore, little nitrite is found in solution if the reactions occur under optimum conditions.

$$O_2 \qquad\qquad\qquad\qquad O_2$$
$$+ \qquad\qquad\qquad\qquad +$$
$$NH_4^+ \xrightarrow[\textit{(Autotrophic)}]{\textit{Nitrosomonas}} NO_2^- \xrightarrow[\textit{(Autotrophic)}]{\textit{Nitrobacter}} NO_3^-$$
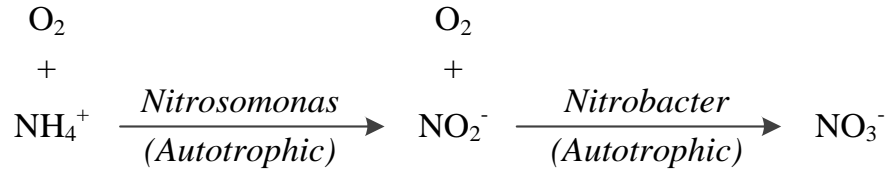
Figure 2-6 Nitrification (Modified from Reddi, 2005)

Denitrification involves the biological reduction of nitrate and/or nitrite to nitrogen gas in the absence of dissolved oxygen. A biological environment with little or no dissolved oxygen but with nitrate or nitrite present is referred to as anoxic. In this process, bacteria use the oxygen contained in the nitrate or nitrite molecules to metabolize organic carbon (USACE, 2001).

Organic carbon
$$+$$
$$NO_3^- \xrightarrow[\substack{\textit{(Facultative/} \\ \textit{Heterotrophic)}}]{\textit{Denitrifier}} NO_2^- \xrightarrow[\substack{\textit{(Facultative/} \\ \textit{Heterotrophic)}}]{\textit{Denitrifier}} N_2^- + CO_2 + H_2O$$
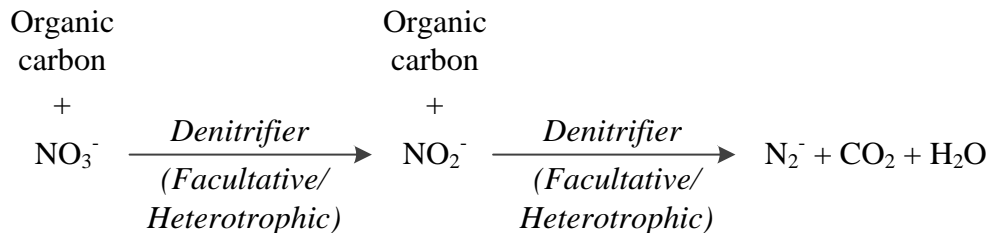
Figure 2-7 Denitrification (Modified from Reddi, 2005)

Unlike nitrification, denitrification is performed by a wide range of heterotrophic bacterial species, many of which are commonly found in typical biological treatment processes-even those not designed to remove nitrogen. These organisms are common because they are facultative and can use oxygen, nitrate, or nitrite as their terminal electronic acceptor. (oxygen source). These organisms will use oxygen preferentially

when it is available, but will change to use nitrate or nitrite whenever dissolved oxygen is in low supply or absent (USACE, 2001).

2.3 Water treatment residual (WTR)

Water treatment residuals (WTRs), the byproducts of drinking water treatment industry, are generated from various treatment processes including coagulation/separation, membrane separation, ion exchange, precipitative softening and granular activated carbon. Presently the coagulation/separation process is still the most common method in water treatment plants (WTPs) and the predominant origin of WTRs (Makris and O'Connor, 2007).

2.3.1 Generation

In the coagulation/separation process of drinking water treatment, metal (usually Fe or Al) salts, together with polyelectrolytes, are added to raw water for the removal of colloids, color, suspended solids and common contaminants. The solids separated from water in the treatment train are collected and concentrated in drying basins, finally resulting in the form of WTRs. Basibuyuk and Kalat (2004) cited an estimation of several million tons of WTRs production in Europe every year, and the amount may double by the next decade. In the U.S., more than 2 million Mg of WTRs are generated from drinking-water treatment industry per day (Prakash and Sengupta, 2003).

2.3.2 Characterization

The compositions and properties of WTRs are different, depending on raw waster qualities and treatment processes. Generally, the compounds in WTR consist of aluminum/ferric hydroxides, polymers, and suspended solids, humic substances and other contaminants removed from raw water (Dayton and Basta, 2001). According to the review of Makris and O'Connor (2007), the particle sizes of dried WTR solids are rarely greater than 2 mm and mostly distributed in the range of 1–5 μm. Depending on the kind of metal salt added, WTRs are categorized into aluminum-based water treatment residual (Al-WTR) and ferric-based water treatment residual (Fe-WTR). Al-WTR commonly has a neutral pH of range of 5.0–8.2 and a total Al concentration range of 15 to 300 g/kg, while Fe-WTR is more alkaline with a pH range of 7.2–9.2, and the total Fe concentration ranges from 109 to 251 g/kg. For all classes of WTRs, high organic matter contents are reported to reach the order of 200 g/kg or more (Makris and O'Connor, 2007).

Babatunde and Zhao (2009) summarized the major elemental chemical composition of the aluminum-based water treatment residual in some previous research studies (Table 2-1).

Table 2-1 Summary for the elemental chemical composition of Al-WTRs

Elemental	References				
contents	Babatunde et	DeWolfe, 2006	Babatunde et	Makris et al.,	Yang et
(mg/g)	al., 2009		al., 2007	2007	al., 2006

Al	42.67	38.3–125.4	15–300	297	121–127
Fe	3.336	16.3–26.1	5–66	102	4.2–4.3
Ca	0.820	4.5–54.6	3–50	29	8.3–8.4
P	0.123	0.5–4.4	0.2–4.4	3.5	-
As	0.034	0.007–0.04	-	-	-
Pb	0.005	0.005–0.032	-	0.04	-
Mg	0.237	0.054–0.142	-	8.9	4.4–4.6
Mn	0.270	0.036–2.688	-	-	-
Ti	0.099	-	-	-	-
Zn	0.03	0.05–0.0017	-	0.03	-
TOC	-	-	8.5–225	-	97.5

Source for the table: modified from Babatunde and Zhao (2009).

2.3.3 Disposal

Since the WTR production from water treatment facilities is enormous all around the world, the treatment and disposal induce significant cost and technical problems. The common disposal options of WTR include directly discharging to surface waters, discharging to wastewater treatment plants, landfilling, and land application (U.S. EPA, 1996).

Unlike wastewater treatment sludges (biosolids), drinking water treatment sludges (WTRs) are exempted in the 40 CFR Part 503 – Standards for the Use or Disposal of Sewage Sludge (U.S. EPA, 1996). In fact, WTRs have not been specifically directed by any established regulations of EPA. The high content of metal in WTRs may induce the concern of potential toxicity. Dayton and Basta (2001) used the toxicity characteristic leaching procedure (TCLP) on selected WTRs and obtained heavy metal levels that were

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significantly less than the TCLP regulatory levels.

In addition, WTRs are classified as one possible source of TENORM (Technologically-Enhanced, Naturally-Occurring Radioactive Material) because the drinking water sources may have contacted with NORMs (Naturally-Occurring Radioactive Materials) and pose radioactive contents of concerned levels. In that case, the radionuclides accumulated WTRs must be specially treated according to the relative guidance (U.S. EPA, 2005), which is beyond the scope of this study. However, most drinking water treatment sludges are thought to have similar radiation levels with typical soils (U.S. EPA, 2005). In sum, excerpt for a few special cases with problematic water sources, WTRs are commonly considered as a non-hazardous material and can be disposed or reused in the environmental-benign ways.

Chapter 3   METHODS AND MATERIALS

Multiple studies have been completed to accomplish the research objectives including (1) characterization of aluminum based water treatment residual (Al-WTR); (2) hydraulic conductivity tests for Al-WTR as a filter media; (3) batch experiments to investigate P sorption on Al-WTR including isotherm analysis; (4) column experiments to study the P sorption capacity in continuous, long-duration operations; and (5) column experiments to study the simultaneous P and N removal from wastewater. In addition, the Method Detection Limits (MDLs) were established for P measurement and standard deviations of replicates were calculated as part of understanding the statistical accuracy and reliability of the analytical measurements.

3.1 Al-WTR solid preparation and characterization

3.1.1 Al-WTR source description

The Al-WTR was obtained from the Loveland Water Treatment Plant in the City of Loveland, Colorado. The water treatment facility utilizes conventional treatment processes to treat the surface water from the Big Thompson River and the Green

Mountain Reservoir. Alum ($Al_2(SO_4)_3 \cdot 14H_2O$) is added as a coagulant for the influent water. WTR with a high content of aluminum and organic matter was generated in the settling and filtration processes, and after concentration was dried in the sludge drying basins. Figure 3-1 shows the process of water treatment and the origins of Al-WTR.
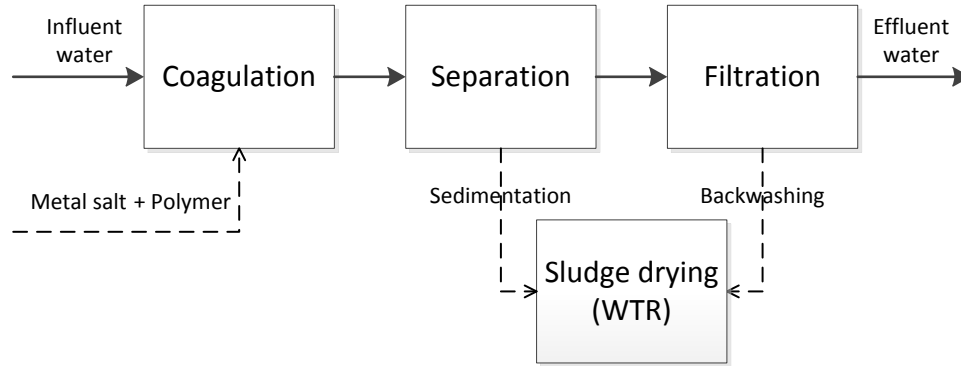
Figure 3-1 Illustration of coagulation/separation process and WTR production

Figure 3-2 shows one of the sludge drying basins with dark-brown colored Al-WTR solid. WTR samples were collected from the surface of the drying basins and shipped to the laboratory with plastic buckets. After that, the Al-WTR solid was air-dried at 20-25 ℃, sieved through 2-mm sieves and preserved in dry and sealed bottles.

Figure 3-2 Al-WTR solid in a sludge drying basin

3.1.2 Characterization

Characterization of the Al-WTR was conducted in the laboratories of Stewart Environmental Consultants, Inc. and the Engineering Research Center at Colorado State University. Important parameters of the material include (1) metal content (esp. Al), (2) organic matter content, and (3) radioactivity. Metal concentrations were determined by acid digestion followed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (EPA Method 200.7). The organic carbon concentration was determined by the combustion method defined in EPA Method 415.1. Total P was measured by Standard Method 4500 (APHA, 1992) which involves acid digestion followed by colorimetric tests.

The total gross alpha was analyzed by a gas-flow proportional counting system (EPA Method 900.0).

3.1.3 Hydraulic conductivity tests

To assess the feasibility of utilizing Al-WTR and sand mixtures in full scale filters, the hydraulic conductivity values were measured by using the constant head method for saturated soils, as identified by Klute et al. (1986). Air dried Al-WTR solid was mixed with sand at ratios of 100% (pure WTR), 80%, 60%, 40% 20%, and 0% (pure sand) respectively to prepare 6 samples of filter media. These samples were packed separately into 6 columns. One end of each column was covered with a piece of cloth to retain the solid. The hydraulic conductivity of the cloth was high enough so that the head loss across it was negligible compared to that across the filter media. With the cloth-covered end down, the columns were set vertically on a rack as illustrated in figure 3-3.
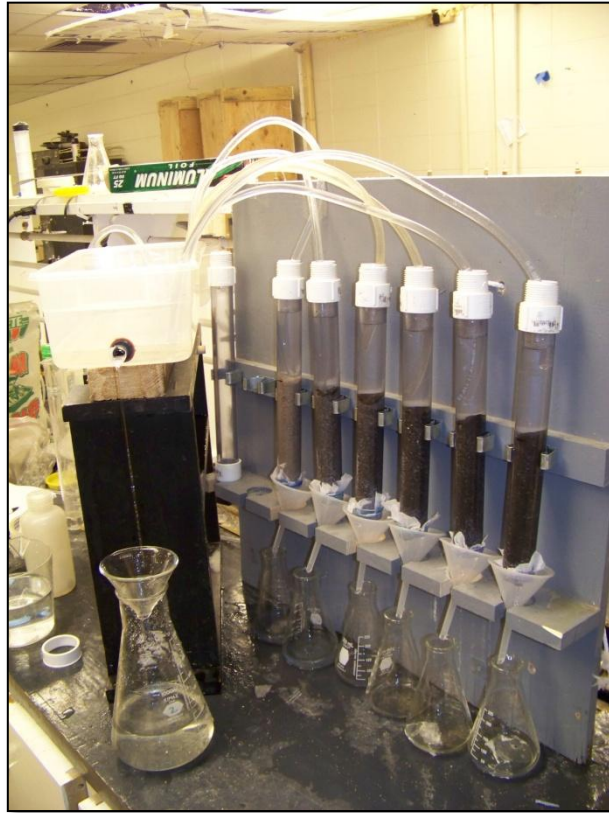
Figure 3-3 Hydraulic conductivity test devices

A water tray was set up with a constant influent flow at one end and an orifice at the

other end to maintain a constant head of water. Water was conveyed from the water tray

to each column by a pipe to create and keep a constant head above the top of samples.

After the water levels on top of the samples and the draining flow had become stabilized,

the percolate was collected in flasks.

Measuring the volume of water, V (mL), which passes through the sample in time, t

(s), and the hydraulic head difference between the water surface and the top of the filter

media, ΔH (cm), the hydraulic conductivity, K (cm/s), was then calculated by

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$$K = \frac{VL}{At\Delta H} \qquad (3\text{-}1)$$

where A (cm^2) and L (cm) are the cross section area and the length of the media column respectively.

3.2 Wastewater description

The wastewater samples used in this study were collected from a WWTP operated by Boxelder Sanitation District, Fort Collins, CO. a aerial view of the WWTP is shown in Figure 3-4. The WWTP utilizes a lagoon system to treat domestic wastewater and has been operated since 1965. The major components include two aerated lagoons, one settling lagoon (not aerated), and chlorination and de-chlorination units. Wastewater samples were collected at the outlet of the last lagoon (settling lagoon) and before the chlorination process.

Figure 3-4 Aerial view of the WWTP operated by Boxelder Sanitation District

The wastewater samples were characterized at the Engineering Research Center of Colorado State University. The parameters of concern in this study are shown in Table 3-1.

Table 3-1 Wastewater characterization

Parameter	Value
Total phosphorus (mg P/L)	2.0-4.9
Orthophosphates (mg P/L)	1.5-3.4
Total nitrogen (mg N/L)	14.0-30.2
Nitrate (mg N/L)	< 0.1
Nitrite (mg N/L)	< 0.1
Ammonium (mg N/L)	14.3-16.2
pH	7.2-7.8
Electronic conductivity (mS/cm)	1.53-1.61

3.3 Batch experiments

Batch sorption experiments were conducted to study the P retention characteristics of the Al-WTR according to the methods identified by Nair et al (1984). Parameters including contact duration, sorbent dosage, and pH, were investigated for their effects on P sorption performance. Also, the maximum sorption capacities for P were estimated at various pH values. The temperature was held constant ($21\pm2^{\circ}$C) during the batch tests.

P solutions used in these experiments include both the wastewater (WW) from Boxelder and a synthetic solution (SS) prepared with D.I. (deionized) water spiked with KH_2PO_4. The characteristics of the WW were shown in Table 3-1. The SS was made with an orthophosphate concentration of 5.0 mg/L (as P).

For this study, RP (reactive phosphorus), which refers to phosphate that responds to colorimetric tests without any hydrolysis or digestion (APHA, 1992), is used to represent orthophosphate. TP (total phosphorus) consists of orthophosphate, condensed phosphate, and organic phosphate. In these experiments, RP was measured by the Ascorbic Acid Method (Method 8048, Hach Co.), and TP was measured by Acid Persulfate Digestion Method followed by Ascorbic Acid Method (Method 8190).

The batch test equipment is shown in Figure 3-5. In the experiments, Al-WTR was placed into 250 ml flasks with 100 mL of either WW or SS and the mixtures were shaken on a rotary shaker (Model # 4626, Lab-line) with a speed of 175 rpm. After the contact duration, the suspensions were withdrawn, filtered through Whatman #42 filter paper, and analyzed for P concentrations in the solution. The difference between the initial concentration and equilibrium concentration was considered as the amount of P retained by the Al-WTR.
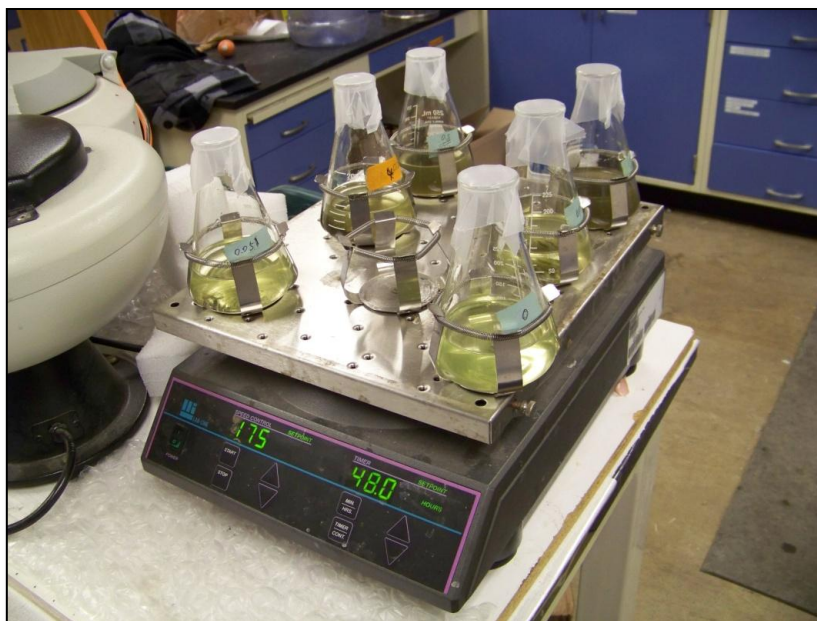
Figure 3-5 Equipment for batch experiments

3.3.1 Equilibrium time determination

In order to determine the equilibrium time of the sorption reaction, different durations of time were used for contacting. Six flasks filled with the same solution and the same dose of Al-WTR solid (6 g/L for each) were prepared and contacted for 12, 24, 48, 96, 120, and 168 hours. Each of the flasks was shaken on the rotary shaker for its contact time, removed and analyzed for residual RP and/or TP in the solution. This experiment was conducted with both SS (RP 5.0 mg/L, TP 5.0 mg/L) and WW (RP 3.4 mg/L, TP 4.0 mg/L).

3.3.2 P Sorption in wastewater

An important objective of this research was to understand if TP from either domestic WW could be adsorbed effectively by the Al-WTR as well as ortho-P. To this end, WW

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(from Boxelder) was used to investigate the sorption performance by the Al-WTR of RP and TP. Also, the effect of sorbent dosage was investigated. Al-WTR doses of 0.5, 1, 2, 4, 6, 10, and 20 g/L were added with 100 mL of WW into flasks and shaken for 48 h (predetermined equilibrium time based on previous experiments). After the equilibrium time, the residual levels in the solutions of both RP and TP were determined.

3.3.3 Effect of pH

pH influences sorption processes by changing the chemical properties of sorbent and sorbate (Pierzynski, 2005) . In the case of the sorption of phosphorus, which is present as an anion, lower pH is often preferable because it enhances the protonation of the functional groups on the surface of the Al oxides (e.g. $O^- \rightarrow OH \rightarrow OH_2^+$), and increases the positive net surface charge (Pierzynski, 2005). pH will also change the form of phosphorus ions in solution. In the general condition of domestic wastewater with a pH range of 6.5 to 8.0 (Hunter and Heukelekian, 1965), when pH is below 7.2, phosphate ions exist mostly in the form of $H_2PO_4^-$, otherwise, the majority form is HPO_4^{2-}. The latter form has the potential to act as a bidentate ligand, and thus may have greater affinity for the sorbent surfaces (Parfitt et al., 1975).

To study the effects of pH on P sorption performance, a series of WTR doses (0.5, 1, 2, 4, 6, 10, and 20 g/L) were mixed with SS (RP 5.0 mg/L) at different pH levels (4, 7 and 9) for 48 h. pH values were adjusted as necessary using hydrochloric acid (0.1 M) and

sodium hydroxide (0.1 M) and the volumes of acid or alkaline added were taken into account in the calculations.

3.3.4 Isotherm analysis

For a given system, the sorption isotherm is the relationship of the sorption density and the equilibrium concentration of the dissolved sorbate at a given temperature (Benjamin, 2002). Sorption isotherms were developed by plotting the sorption density values versus the equilibrium concentrations of the sorbent (phosphate).

For a system in equilibrium, the sorption density (Q, mg/g) is computed as:

$$Q = \frac{C_0 - C_e}{C_{solid}} \qquad (3\text{-}2)$$

where C_0 is the initial concentration of sorbate in solution (mg/L), C_e is the equilibrium concentration of sorbate (mg/L), and C_{solid} is the dose of sorbent (g/L). Equation (2) can also be written as:

$$C_{solid} = \frac{C_0 - C_e}{Q} \qquad (3\text{-}3)$$

With the relationship of Q and C_e described by the isotherm, for any values of given initial concentration (C_0) and equilibrium concentration (C_e), the required sorbent dose (C_{solid}) can be estimated. (Benjamin, 2002)

In addition, the P sorption process was quantified with Langmuir and Freundlich isotherm analyses. Langmuir and Freundlich isotherms are the two most widely used models for sorption characterization (Benjamin, 2002). The Langmuir isotherm is

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described as:

$$Q = \frac{Q_{max}KC_e}{KC_e+1} \tag{3-4}$$

where Q_{max} (mg/g) is the maximum sorption density and the constant K is related to binding energy. The linearized form of Equation (3-4) can be written as:

$$\frac{C_e}{Q} = \frac{1}{Q_{max}}C_e + \frac{1}{K}\frac{1}{Q_{max}} \tag{3-5}$$

Therefore, the values of Q_{max} and K were calculated from the slopes and intercepts generated from a plot of C_e/Q and C_e.

The Freundlich isotherm takes the form of:

$$Q = K_d C_e^{\frac{1}{n}} \tag{3-6}$$

where K_d ((mg g^{-1})(L mg^{-1}) n^{-1}) and n are fitting experimental parameters, dependent on material characteristics and considered constant for each sorbent and sorbate group. The constant K_d is often used to evaluate the sorption capacity. The linear form can be written as:

$$\log Q = \log K_d + \frac{1}{n}\log C_e \tag{3-7}$$

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.

3.4 Column experiments

Continuous-flow column tests for P and N removal were conducted with filter media packed columns in the laboratory. The filter media used included sand, Al-WTR and

mixtures of the two with different proportions. Clear PVC pipes were utilized as the columns, and each of them had a length of 30.5 cm and an inner diameter of 2.5 cm. In order to prevent photosynthesis and algae growth in the filter media, foil was used to cover the columns and shield the light from outside. A view of column tests is shown in Figure 3-6.

Figure 3-6 Equipment for column experiments

After being filled with filter media, the columns were capped on both ends to hold the solid and set up vertically. The feed water, which was preserved in 4-liter tanks, was pumped by a peristaltic pump (MasterFlex® L/S®, Cole-Parmer) to pass through the

columns in a continuous and up-flow manner with saturation conditions in the filter media throughout the testing period.

Two sets of column experiments were conducted with different purposes. Column Experiment I was a long-duration test run with synthetic P solution (SS), aiming to estimate the P sorption capacity under continuous-flow conditions for a 2 month period. Column Experiment II investigated the simultaneous P and N removal in WW through the filters.

3.4.1 Column Experiment I: P sorption study

This experiment was designed as a long duration operation to investigate the P removal efficiency and breakthrough characteristics by filter media with various proportions of Al-WTR. Five columns were set up with Al-WTR amendment ratios of 0, 5%, 10%, 15%, and 20% by volume in their filter media respectively. The features of the columns are shown in Table 3-2. The feed water for the tests was P-spiked raw water from a surface water source. The raw water was collected from Horsetooth reservoir (Fort Collins, CO.), which had a negligible background level of P (TP < 0.3 mg/L), and was spiked with KH_2PO_4 to create an RP concentration of 3.7 − 4.5 mg/L. The synthetic feed water was passed through the column at an average flow rate of 0.36 mL/min for over two months. Phosphate concentrations in the effluent were measured approximately once every 14 pore volumes of water passed.

Table 3-2 Column specifications for long-duration experiment

Column ID	C0	C5	C10	C15	C20
WTR (%)	0	5	10	15	20
Sand (%)	100	95	90	85	80
Hydraulic retention time (HRT) (d)	0.112	0.112	0.112	0.112	0.112
Hydraulic loading rate (HLR) ($m^3\ m^{-2}d^{-1}$)	1	1	1	1	1

3.4.2 Column Experiment II: simultaneous P and N removal study

This experiment aimed to investigate the simultaneous P and N removal performances in two different filter media types (Al-WTR and sand) and two different solutions (wastewater and deionized water). As a result, this experiment was designed as a 2×2 factorial.

The wastewater samples used in this experiment were from the same source (Boxelder) as in the batch tests. $NaNO_3$ solid was added into the wastewater to increase the nitrate levels to approximately 15.0 mg NO_3-N/L. Correspondingly, synthetic solution was made to have similar phosphate and nitrate concentrations (ortho-P 2.4 mg/L and nitrate 15.1 mg /L in average).

The combination of filter media and solutions are shown in Table 3-3. During the experiment, the column influents and effluents were routinely monitored for TP, RP, NO_3-N, NH_3-N, TOC, TN, pH and electrical conductivity (EC).

Table 3-3 Column specification for simultaneous P and N removal experiment

Column ID	Sand-WW	WTR-WW	Sand-SS	WTR-SS
Filter media	Sand	WTR	Sand	WTR
Porosity	0.4	0.6	0.4	0.6
Feed water	wastewater	wastewater	synthetic solution	synthetic solution
Flow rate (min/L)	0.31	0.31	0.33	0.31
HRT (d)	0.134	0.134	0.126	0.134
HLR (m^3/m^2d)	0.91	0.91	0.97	0.91

3.5 Analytical measurements

The measurement methods for major parameters in this study are listed in Table 3-4.

Table 3-4 Summary of measurement methods

Parameter	Measurement method	Apparatus
RP	Ascorbic Acid Method (Method 8048)	Spectrophotometer DR/2500 (Hach Co.)
TP	Acid Persulfate Digestion Method and then measured by Ascorbic Acid Method (Method 8190)	
NO_3-N	Cadmium Reduction Method (Method 8039)	
NH_3-N	Salicylate Method (Method 10031)	
TC		TOC analyzer TOC-VCSH, (Shimadzu Co.)
IC	Combustion catalytic oxidation/NDIR method	
TN		
pH	pH probe	AR25, Fisher Scientific
EC	Conductivity meter	AB30, Fisher Scientific

3.6 Quality control and statistical analysis

The method detection limit (MDL) for P measurement in our lab was determined according to the method identified by the EPA (40 CFR 136 Appendix B). MDLs were

calculated in order to understand the accuracy of the analytical measurements and help

define the lower range of the test method. The MDL was determined by the following

procedure: first test a solution that has a concentration of one to five times the estimated

detection limit for seven or more times, and then determine the standard deviation of the

data set. The method detection limit is calculated as:

$$MDL = TS \qquad (3\text{-}8)$$

Where T is Student's t value the student's t value at a 99% confidence level and a

n-1 degrees of freedom (n is the number of times the solution was measured). S is the

standard deviation.

In this study, the 10-time tests conducted for RP measurement showed an average

concentration of 0.198 mg/L for a nominal RP concentration of 0.20 mg/L, with a

standard deviation of 0.0215 mg/L. MDL for phosphorus concentration was observed to

be 0.06 mg/L. This implied that concentration values of 0.061 mg/L or higher were

measured and reported with 99% confidence that the concentration is greater than zero.

The test data are presented in Table 3-5.

Table 3-5 Test data for Method Detection Limit determination

Times	1	2	3	4	5	6	7	8	9	10
RP (mg/L)	0.17	0.17	0.21	0.19	0.24	0.19	0.20	0.20	0.22	0.19
Average (mg/L)					0.198					
Standard deviation					0.021					
Student's t value					2.821					
MDL (mg/L)					0.061					

Chapter 4   RESULTS AND DISCUSSION

4.1 Al-WTR characterization

Table 4-1 presents the results for the Al-WTR chemical and physical characterization. The Al content in the Al-WTR was about 1–5 orders of magnitude greater than the other elements analyzed. The aluminum value was comparable to other WTR materials reported by other researchers including Babatunde et al. (2009) (42.67 mg/g), DeWolfe (2006) (38.3-125.4 mg/g), Makris and O'Connor (2007) (15-300 mg/g), Babatunde and Zhao (2007) (297 mg/g for the largest).

Table 4-1 Chemical and physical properties of Al-WTR

Parameter		Value	Unit
Metal	Aluminum	1.1×10^5	ppm
	Iron	1.7×10^4	ppm
	Arsenic	7.64	ppm
	Barium	98.4	ppm
	Cadmium	0.285	ppm
	Calcium	7210	ppm
	Lead	<1	ppm
	Magnesium	2840	ppm
	Potassium	2010	ppm
	Selenium	1.95	ppm
Phosphorus	Total Phosphorus	995	ppm
Carbon	Total Carbon	8.06	%
	Total Organic Carbon	7.80	%
	Total Inorganic Carbon	0.26	%
Total gross Alpha		8.5	PCi/g
Density	Bulk density	0.83	g/cm
	Particle density	2.05	g/cm
Porosity		0.6	
pH		6.8-7.1	
EC		2.1	mS/cm

4.2 Hydraulic conductivity results

The hydraulic conductivity results of Al-WTR and sand mixtures with different ratios are presented in Figure 4-1. The pure sand sample demonstrated the highest hydraulic conductivity. Although Al-WTR has a larger porosity than sand, a lower hydraulic conductivity was observed in the Al-WTR sample. When the proportion of WTR increased, hydraulic conductivity dropped. However, the lowest hydraulic conductivity was not observed at the pure Al-WTR one, but in the range of 60–80% of

Al-WTR proportion. That may because the mixing of two materials with different particle sizes reduced the porosity to be lower than each one of the originals, and the substitute Al-WTR content released water slower than sand.
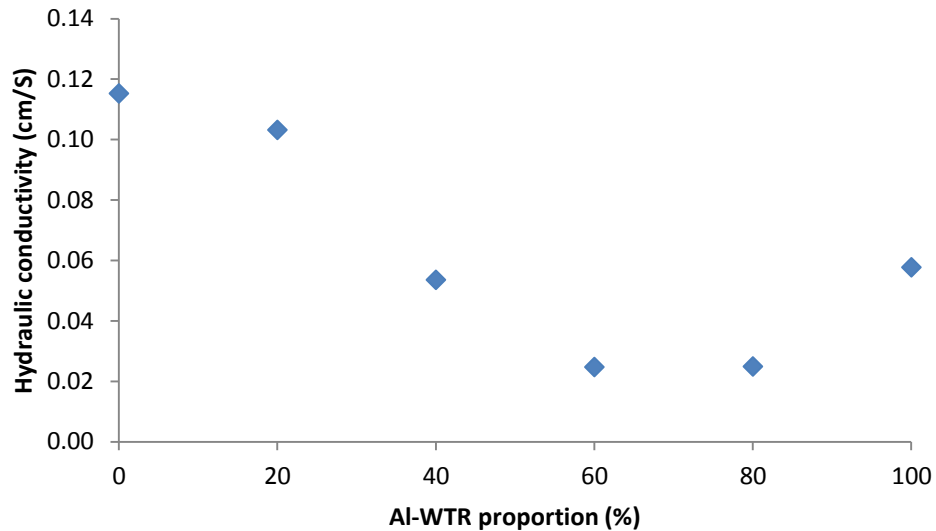
Figure 4-1 Hydraulic conductivity variations of Al-WTR – sand mixtures with different mixing ratios

From a practical perspective, it is beneficial for filter media to have higher hydraulic conductivities, which allow higher hydraulic loading rates and larger treatment capacities. On the other hand, materials with low hydraulic conductivities could easily induce troubles like clogging. According to the ranges of the common intrinsic permeability values for solid materials (Figure 4-2), Al-WTR and the sand mixtures all demonstrated acceptable hydraulic conductivities, which provides the potential for practical use as filter media.

K (cm/s)	10^2	10^1	10^0=1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}
K (ft/day)	10^5	10,000	1,000	100	10	1	0.1	0.01	0.001	0.0001	10^{-5}	10^{-6}	10^{-7}
Relative Permeability	Pervious				Semi-Pervious				Impervious				
Aquifer	Good				Poor				None				
Unconsolidated Sand & Gravel	Well Sorted Gravel		Well Sorted Sand or Sand & Gravel		Very Fine Sand, Silt, Loess, Loam								
Unconsolidated Clay & Organic					Peat		Layered Clay		Fat / Unweathered Clay				
Consolidated Rocks	Highly Fractured Rocks				Oil Reservoir Rocks		Fresh Sandstone		Fresh Limestone, Dolomite			Fresh Granite	

Figure 4-2 Ranges of common intrinsic permeability
(http://en.wikipedia.org/wiki/Hydraulic_conductivity)

4.3 Batch experiments

4.3.1 Equilibration time determination

Figure 4-3 shows the profiles of P concentration in the synthetic solution (SS) and

the wastewater (WW) after different contact durations with the Al-WTR solid (6 g/L).

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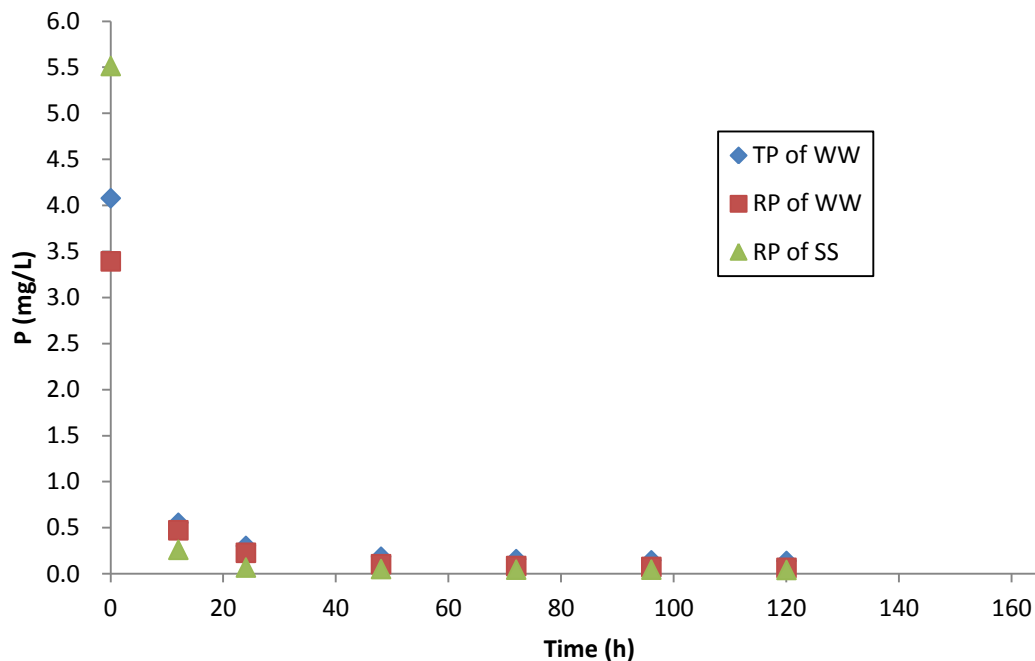
Figure 4-3 P concentration at different contact times

All cases illustrated a similar trend. The initial rapid rate of sorption decreased with time, giving way to a very slow rate of approach equilibrium over a long duration. The results validate the theory that the P sorption is a "biphasic" reaction as mentioned above (Pierzynski et al., 2005). After 48 h, although the sorption process did not literally stop, the amount of removal was marginal. Accordingly, from a practical perspective, the duration of 48 h was adopted as the equilibrium time to conduct the subsequent experiments.

4.3.2 P sorption in wastewater

The sorption performances of different P species by the Al-WTR were investigated with various dosages of the sorbent in 48-hour batch reactions.
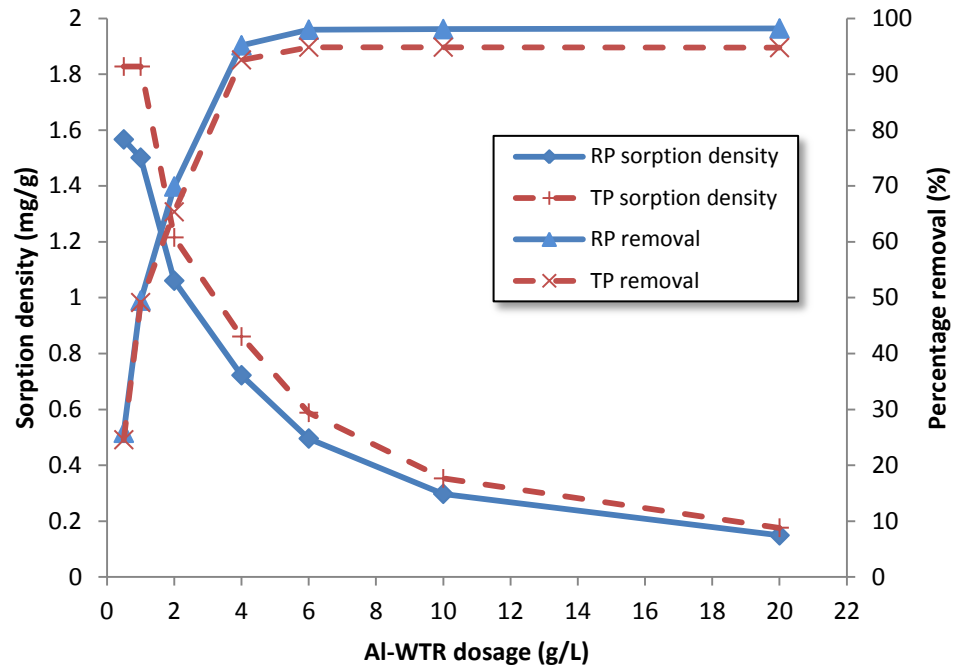
Figure 4-4 Effect of Al-WTR dosage on the sorption density and removal rates of RP and TP
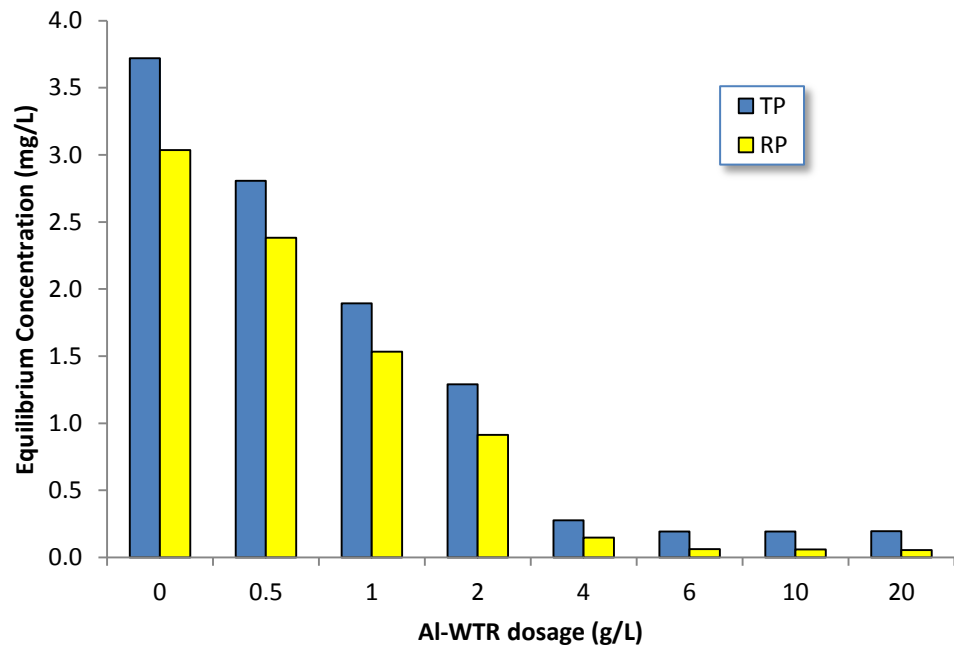
Figure 4-5 Equilibrium concentrations of RP and TP for different Al-WTR dosages

The data shown in Figures 4-4 and 4-5 reveal how the variation of sorbent dosages influences the retention performance of P (both TP and RP) in the given system. When the sorbent dose was below 4 g/L (including 4 g/L), the increase of Al-WTR dose steadily reduced the equilibrium concentration of P species, in other words, increased the P retention ratio, suggesting that phosphorus sorption was primarily limited by the availability of the sorption sites on the surface of Al-WTR solid in this phase. However, at doses beyond 6 g/L (including 6 g/L), the effect of Al-WTR increase on P retention became marginal and equilibrium concentration could not be significantly reduced further. A possible explanation is that when the P concentration dropped to a certain level in the solution, although there were still abundant sorption sites, the driving force for sorption reaction was greatly reduced and the sorption - desorption process tended to reach an equilibrium state. This phenomenon is helpful to estimate the lowest equilibrium concentration of sorbates.

The results demonstrated good removal efficiency for both RP and TP by Al-WTR solid with adequate dosage. When the sorbent dosage reached or exceeded 6 g/L, 95% of RP and 90% of TP could be removed, and equilibrium concentrations of about 0.06 mg RP/L and 0.20 mg TP/L could be achieved. As illustrated in Figure 4-4 and 4-5, on the one hand, RP (representing orthophosphate) had lower equilibrium concentration and higher removal ratio than TP; on the other hand, TP had higher sorption densities than RP.

As a result, it can be concluded that the Al-WTR can efficiently remove phosphorus both in orthophosphate and other forms in the wastewater, but is more effective for orthophosphate retention than for TP. Accordingly, in the application of WW treatment, it would be preferable to convert total P into the orthophosphate form as much as possible before the sorption process.

4.3.3 Isotherm Analysis at different pH

The RP sorption isotherms in SS with different pH values of 4, 7, and 9 were plotted and are presented in Figure 4-6. In all three cases, it was observed that the sorbents had high affinities for P. Although the pH value that had the best sorption condition had not been determined, the cases with lower pH demonstrated better sorption behaviors, which implied lower pH conditions were preferable for P removal. This conclusion is consistent with other researchers (Mortula and Gagnon, 2007, Pierzynski et al., 2005). However, even in the case of a pH of 9, the sorption capacity was still relatively high. Accordingly, the results of isotherm analysis proved a good robustness of P sorption process at a wide range of pH levels.
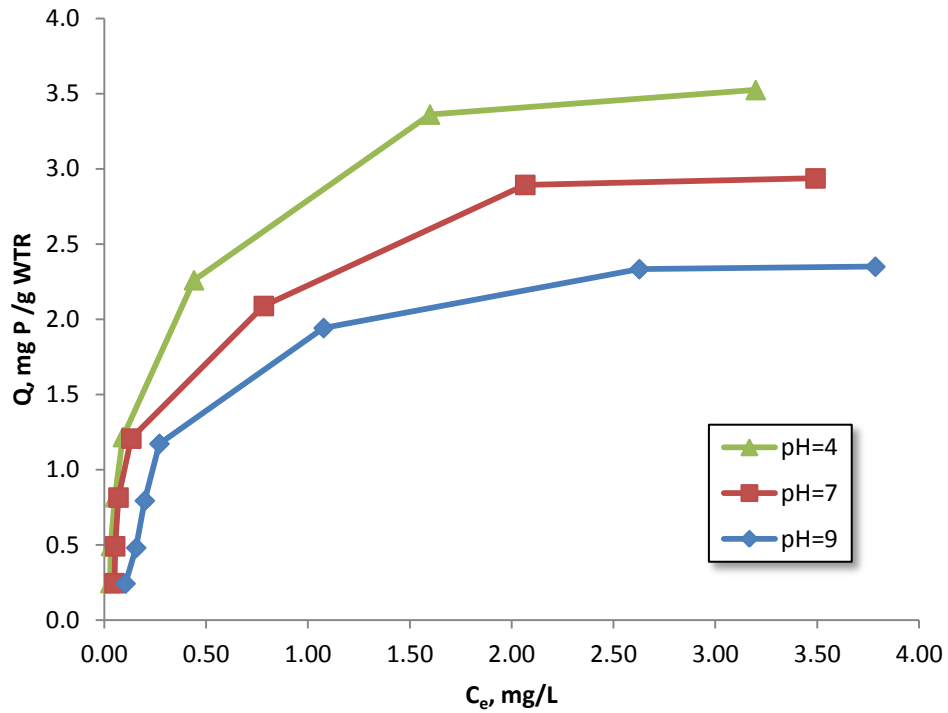
Figure 4-6 P Adsorption isotherm at different pH values

Linear forms of Langmuir and Freundlich Isotherm equations are plotted and shown

in Figures 4-7 and 4-8 respectively to analyze for the sorption coefficients. The calculated

coefficient results are presented in Table 4-4. According to the values of R^2, the date of

experimental results fit the Langmuir behavior better than the Freundlich equation. Both

of the two demonstrated the best P sorption behavior at the pH of 4, followed by 7, and 9.

These results are comparable to those from other researchers. For example, Yong et al.

(2006) reported a Q_{max} range of 0.7 to 3.5 mg P/g when pH was varied from 9.0 to 4.3;

Mortula and Gagnon (2007) reported a Q_{max} for RP of 3.212 mg/g and TP of 0.538 mg/g

for a wastewater with a pH of 7.23.
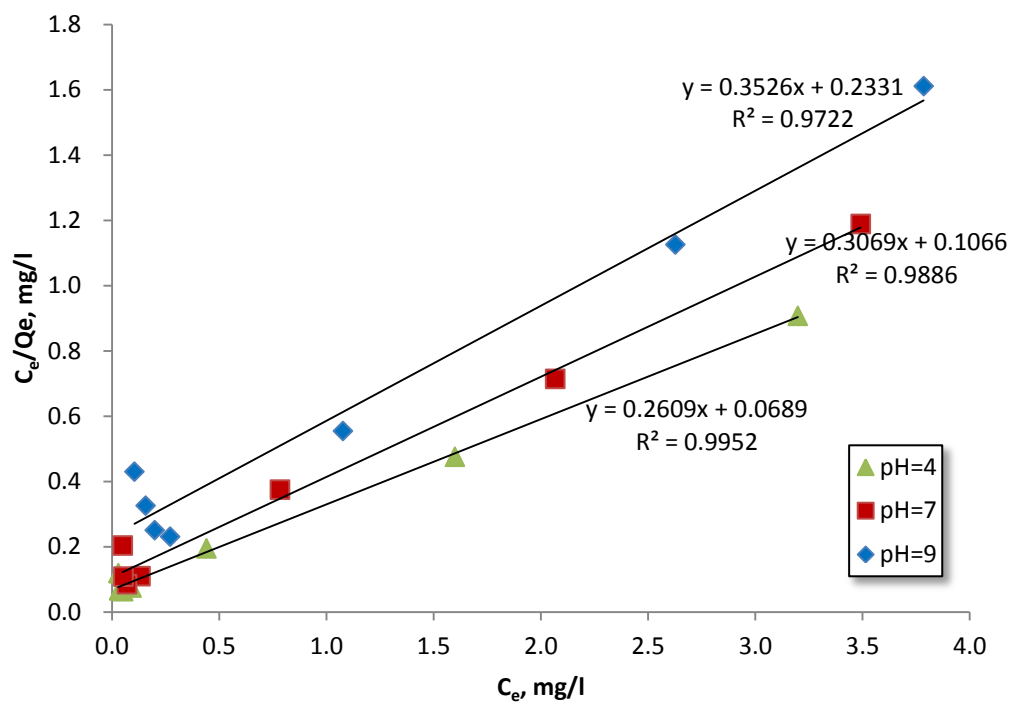
Figure 4-7 Linear form of Langmuir isotherm equations
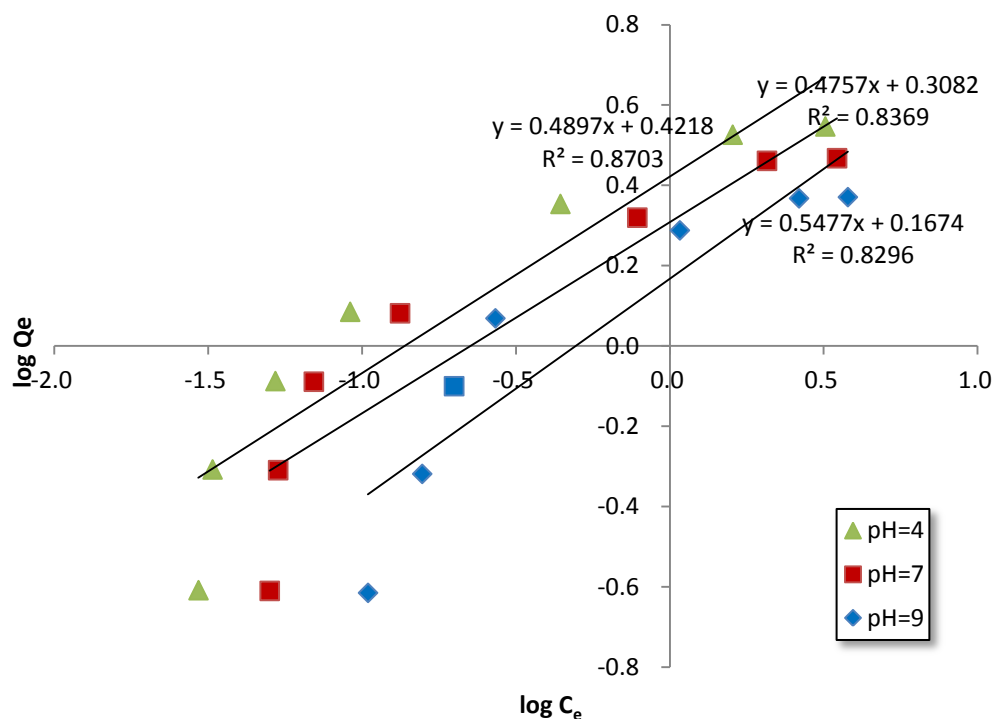
Figure 4-8 Linear form of Freundlich isotherm equations

Table 4-2 Coefficients of Freundlich and Langmuir adsorption isotherms

pH	Langmuir			Freundlich		
	Q_{max} (mg/g)	b	R^2	Kd ((mg/g)(L/mg) (1/n))	n	R^2
4	3.833	3.511	0.995	2.641	2.042	0.870
7	3.258	2.879	0.989	2.033	2.102	0.837
9	2.836	1.513	0.972	1.470	1.826	0.830

4.4 Column experiments

4.4.1 Column experiment I: phosphorus sorption study

For a porous material, the pore volume is defined to be equal to the total volume

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subtracted by the material volume. The concept of pore volume number (n) was used in this study to measure the amount of feed water passed through the filter media. In the column tests, the pore volume numbers (n) were calculated as Equation (4-1).

$$n = \frac{Q}{Vp} \qquad (4\text{-}1)$$

where Q is the total volume of the water passed the column, V is the volume of the empty column and p is the porosity of the filter media.

Figure 4-9 shows a plot of the RP removal rates through the columns as a function of pore volumes of feed water. As illustrated, the P removal rate in column C0 (sand) demonstrated a fast drop from the beginning and soon approached zero. It indicated the P sorption capacity of the sand was quickly exhausted, and the sorption amount of P was insignificant. The results also implied that as the background, the contribution of sand on P sorption is negligible in column C5 (5% WTR), C10 (10% WTR), C15 (15% WTR) and C20 (20% WTR).

In the column sorption tests, constant and high removal of P could be maintained until certain pore volumes were reached, and after that, removal rates started to drop significantly. The number of pore volumes was defined as the breakthrough pore volume (BPV) and the point where breakthrough took place in the curve was defined as the breakthrough point (BP). In columns C5, C10, C15 and C20, it could be observed that the proportion of Al-WTR had a clear influence on the length of BPV, but did not

significantly affect and removal rates and effluent concentrations before the BP. The

column data of columns before BPs appeared are summarized in Table 4-5.
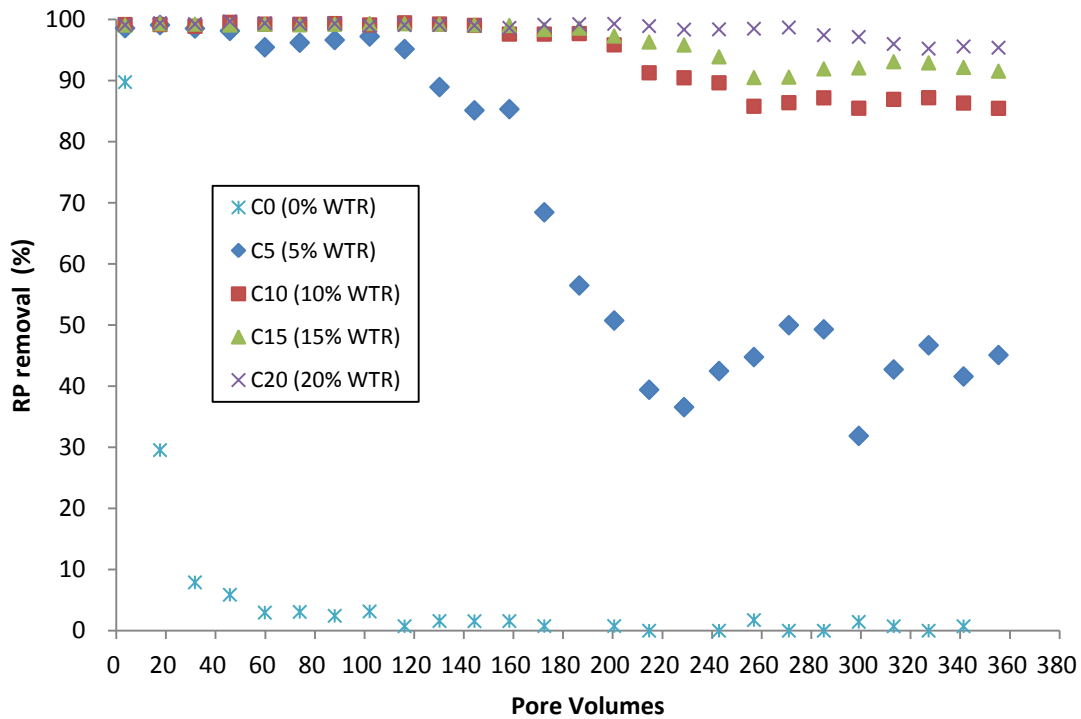
Figure 4-9 RP removal rates through the columns as a function of pore volumes

Table 4-3 Summary of the data for the columns before the BPVs (Mean values)

Column ID	C5	C10	C15	C20
BPV	60	158	201	285
C_e (mg/L)	0.06	0.03	0.04	0.04
Removal rate (%)	98.6	99.2	99.1	99.1
Sorption density (mg/g)	12.79	18.20	15.55	16.43

Unlike C0, none of the filter media in C5 − C20 was exhausted (P removal rate

dropped to zero) until the end of the experiment. This phenomenon was possibly due to

the "biphasic" sorption mechanism discussed previously. The rapid sorption phase took

place before the BP, while after the BP, although not as effective as before, the slow

sorption phase could still achieve P removal.

According to the results of this experiment, the BP appeared when the sorption

density of Al-WTR reached 15.74 ± 2.26 mg/g (mean $\pm$ S.D.). This provides a basis for

the lifetime estimation for the fixed-bed filter design in full-scale applications. The

sorption density results, even if the media had not been fully saturated, however, were

different than the maximum sorption density data obtained in batch tests, which is 2.84 –

3.83 mg/g. The significant difference is mainly due to the continuous flow that has a

greater diffusion driving force than batch conditions (Yang, 2003). During the continuous

contact of solution and sorbent, the concentration gradient could be maintained until the

breakthrough point reached, while in the batch condition, the concentration gradient

between solution and sorbent quickly goes down as the sorption process takes place and

impedes the progress of further sorption. Another reason may be the 48-hour equilibrium

time in the batch tests was not long enough. Longer contacting time, 6 days, 12 days,

even 80 days (Makris et al., 2005) had been conducted in other studies. The slow reaction

phase of sorption can last for a long duration and the maximum P sorption capacity

cannot be estimated properly via isotherm method if the equilibrium state is not reached.

The inconsistency in the sorption capacity between batch and continuously-flow results

was also reported by Yang et al. (2006) suggesting the theoretical batch-test estimation

may not be able to represent the real situation in continuous flow or other scenarios.

4.4.2 Column experiment II: Simultaneous phosphorus and nitrogen removal study

The effluent concentrations and the removal rates of P and N were analyzed along with the number of pore volumes. The experimental data are presented in Appendix.

4.4.2.1 Nitrogen removal study

The data presented in Figure 4-10 compares the removal rates of NO_3-N in different columns. In each of the columns, the removal performances eventually reached a relative steady-state condition after initial fluctuation. The fluctuating phase should represent the process of biofilm acclimation while the stable phase reflected the N removal performance after the full development of biofilm and the stabilization of a biological denitrification process. Although the duration of the fluctuating phase was variable, it appears the stable phase was reached after proximately 60 pore volumes in all the cases.
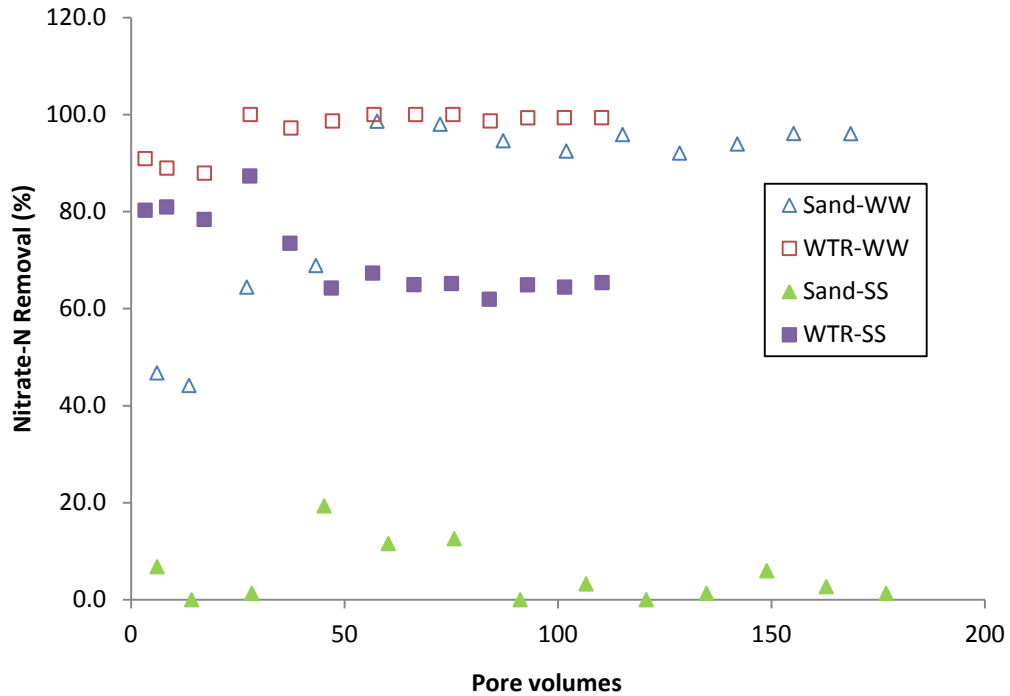
Figure 4-10 NO$_3$-N removal in column tests

In the stable phases, the average removal rates in the columns followed the sequence as Sand-SS (3.4%) < WTR-SS (64.8%) < Sand-WW (94.9%) < WTR-WW (99.4%). Generally, the columns fed with SS demonstrated lower denitrification efficiencies than the ones feed with WW. Based on the similar anoxic condition as designed in the columns, the difference of denitrification efficiencies could be due to the availability of organic carbon (OC) sources (electron donor). For biological denitrification, although the denitrifiers include both heterotrophic and autotrophic bacteria, the reactions are primarily performed by heterotrophic processes, in which an OC source is required (Carlson and Ingraham, 1983).

In the case of Sand-SS, NO_3-N was minimally removed (about 3.4% removal) and denitrification was limited by OC in the solution. However, with the same feed water (SS), WTR-SS had a much lower C_e than Sand-SS. The reason may be due to the WTR acting as a source of OC to the biofilm. As illustrated in figure 4-11, in the acclimated filter media, solid particles or carriers are covered with biofilm, where biological denitrification occurs. An OC source that supports the denitrification process can be obtained from either the outside solution or the inside solid substrate. In the case of Sand-SS, the feed water SS (made out of D.I. water) didn't possess organic matter and the sand surface was poor in organics also. Hence heterotrophic denitrification could not be sustained. In contrast, the Al-WTR in the column WTR-SS had a high content of organic matter, which could be slowly released and supplied as the carbon source for denitrification.

As the results indicated in this study, denitrification with 60 - 70% NO_3-N removal was achieved in the Al-WTR even without the carbon source from outside solution (WW). Based on the same assumption, in the cases of Sand-WW and WTR-WW, when the carbon source from the solution was available, it is possible that the biofilm in WTR-WW was able to obtain OC from both inside substrate and outside solution and thus be more efficient than the one in Sand-WW. This phenomenon is especially meaningful for improving denitrification treatment processes using wastewater with low levels of BOD

(e.g. secondary effluent), in which a supplemental carbon source is required. Al-WTR

filters can achieve better removal efficiency in a low-carbon solution while reducing the

demand of a supplemental carbon source.
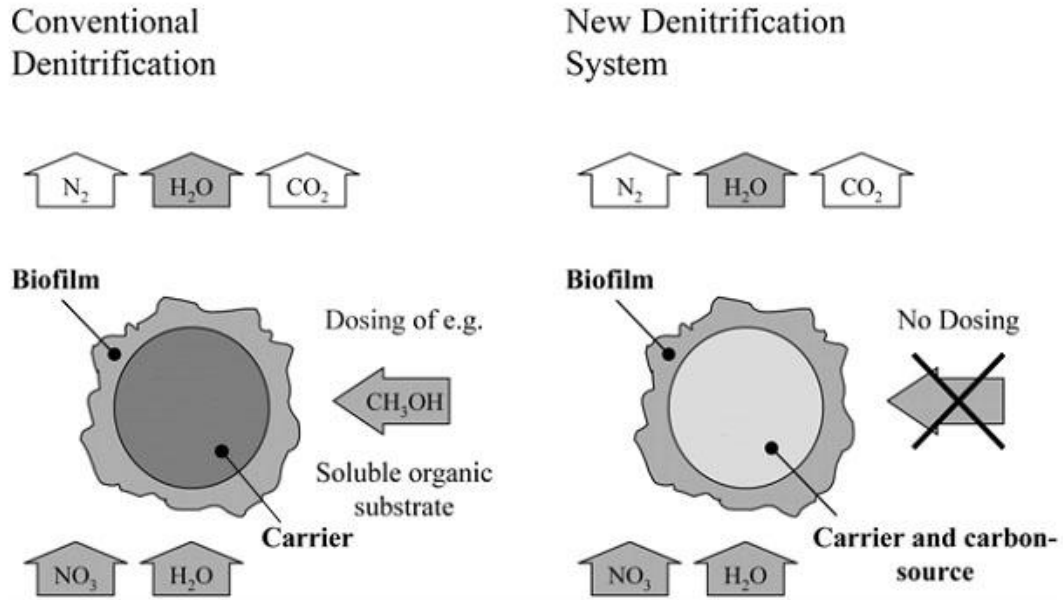
Figure 4-11 Carbon sources for denitrification from different ways
(Modified from Della Rocca et al., 2005)

Also, as illustrated in Figure 4-10, the fluctuating phase was longer in column

Sand-WW (about 60 pore volumes) than column WTR-WW (about 30 pore volumes),

indicating the biofilm in Al-WTR acclimated faster than in sand. This observation may be

due to the assumption that obtaining OC was more efficient from both inside and outside

and thus the biofilm growth was faster. However, this assumption needs to be verified

with more studies in the future. This discovery can be beneficial to Al-WTR applications

in fixed-bed filters. In a fixed-bed filtration process, backwashing would disrupt the biofilm on the filter media, and the time required for re-acclimation will be critical. The faster formation of new biofilm in Al-WTR applied filter media can potentially reduce the interval time and optimize the sorption/denitrification process for WW treatment.

4.4.2.2 Phosphorus removal study

Figure 4-12 shows the column effluent concentrations of RP and TP as a function of pore volume. The P effluent concentrations and removal rates through the columns were analyzed and are presented in Table 4-7. The results were consistent with those obtained from Column Experiment I. On the one hand, the sorption capacity was quickly exhausted in sand columns. On the other hand, low levels of P in the effluent were consistently observed in Al-WTR columns. It is notable that with the same feed water (SS), the P removal efficacy of column WTR-SS (C_e = 0.03 mg P/L, removal rate 98.9%) was similar to the results in Column Experiment I (C_e = 0.03 − 0.06 mg P/L, removal rate 98.6-99.2%), although WTR-SS has a higher WTR content (100%). This proves again that the WTR content in the filter-media mixture does not affect the P removal efficacy directly.
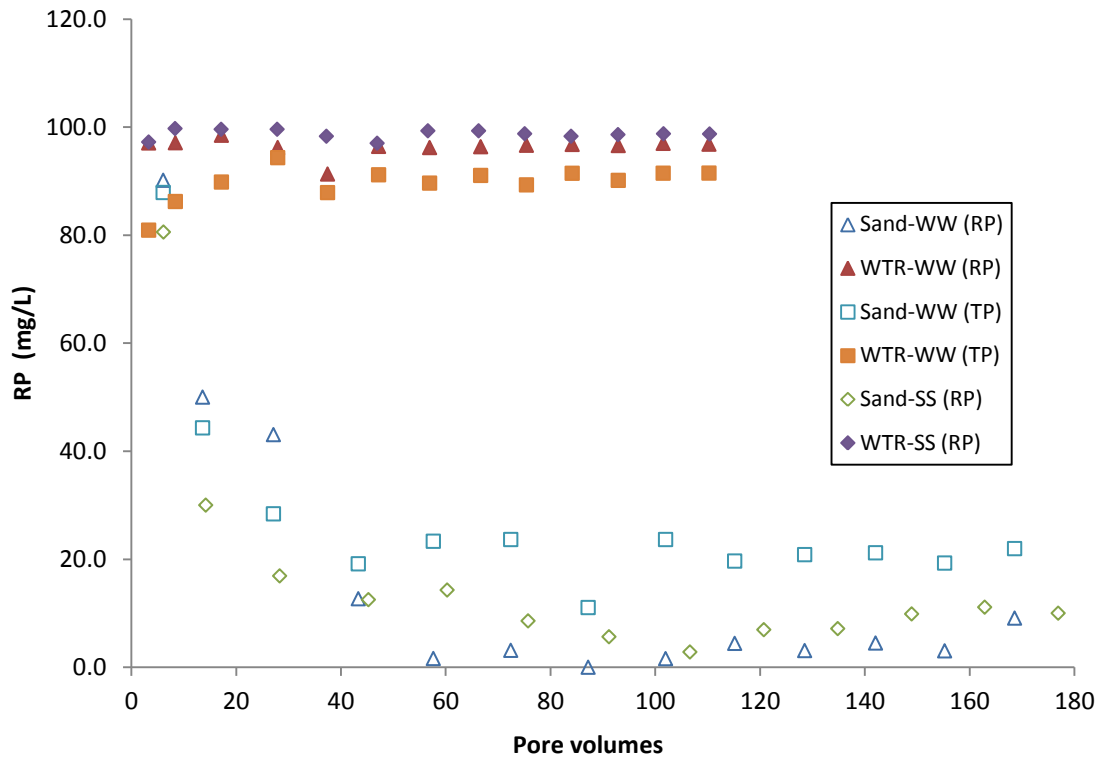
Figure 4-12 Removal of RP and TP in column tests

Table 4-4 Summary of P concentrations through columns (mean $\pm$ S.D.)

Parameter		Sand-WW	WTR-WW	Sand-SS	WTR-SS
RP	C_0 (gm/L)	2.18	2.18	2.31	2.31
	C_e (gm/L)	1.87	0.08	2.04	0.03
	Removal (%)	2.3	96.2	7.6	98.9
TP	C_0 (gm/L)	2.64	2.64	–	–
	C_e (gm/L)	2.02	0.26	–	–
	Removal (%)	23.8	90.1	–	–
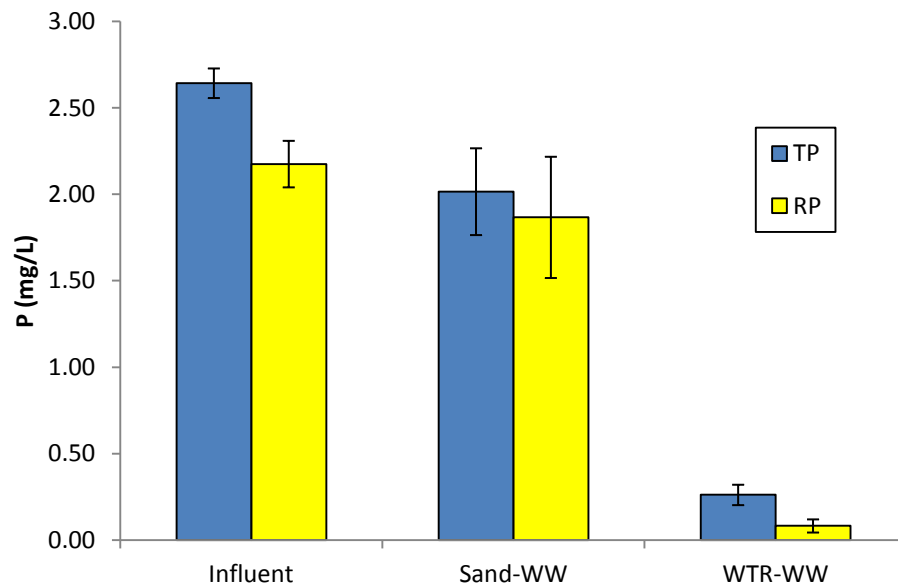
Figure 4-13 Effluent concentrations of different P species (error bar = standard deviation)

Figure 4-13 compares the effluent concentrations of different P species between Sand-WW and WTR-WW. On the one hand, RP removal was remarkably improved in Al-WTR compared with sand. On the other hand, the difference in TP was not as much as in RP. This result implies that the removal of the organic P using Al-WTR was not as efficient as orthophosphate removal. Razali et al. (2007) had proved the adsorption capacity for different P species follows the sequence of orthophosphate > polyphosphate > organic phosphate. This phenomenon was possibly because comparing to orthophosphate ions, the bigger molecular weight of condensed phosphate and organic phosphate molecules induces a slower diffusion rate and the affinity between sorbate and solid surface is weakened (Razali et al., 2007). As a result, in wastewater treatment practices, a

better removal efficiency can be achieved by transferring other forms of P into orthophosphate as much as possible.

4.4.2.3 TOC leaching levels

The OC in the columns is significant to the denitrification process. The Effluent TOC levels over time were plotted in Figure 4-14. It indicates that high level of organic matter (OM) was flushed from the WTR in the first $20 - 30$ pore volumes, but after that, the OM leaching approached a steady state. In each pair of columns that has the same feed water, there is an elevated TOC level in the column packed with WTR than the one with sand. The elevation of TOC (about $20 - 40$ mg/L), which is beneficial to denitrification, is due to the contribution of WTR. Also, the release of OM from WTR over time seems to be slow and consistent. Yarkin's research (2008) that conducted continuous operation over a long period of time proved that constant OM leaching persisted for over 12 months. As a result, it can be expected that the P adsorbing capacity of the WTR will be exhausted before the OM leaching, and the simultaneous P and N removal can be maintained.
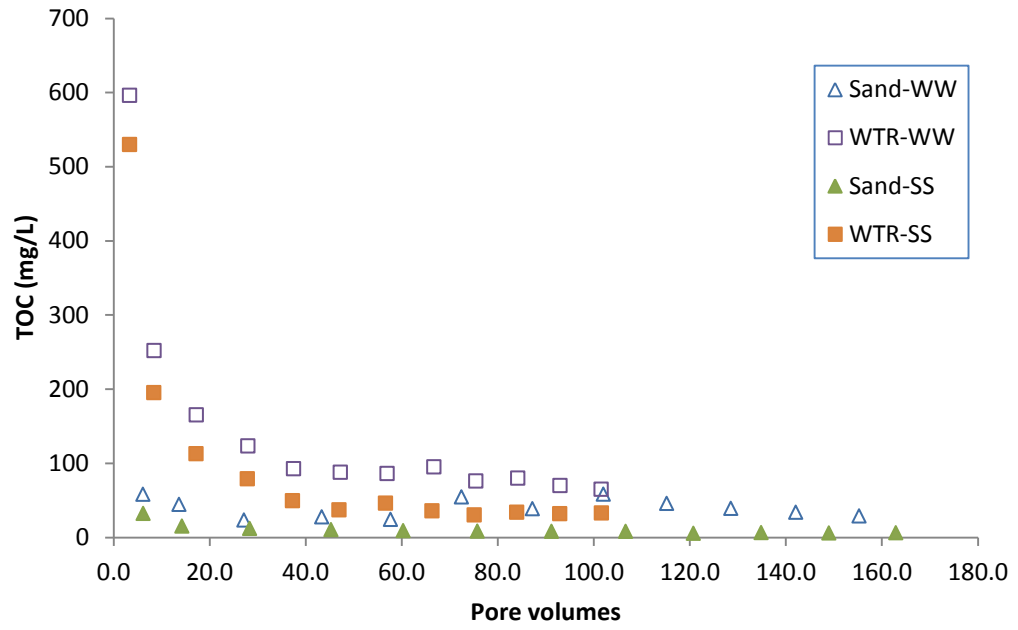
Figure 4-14 TOC leaching levels over time

Chapter 5   BENEFICIAL USE OF WTR FOR NUTRIENT CONTROL

Substantial focus is now being placed on nutrient control by a variety of state and federal regulatory agencies. Challenges lie in the N and P control in small-scale wastewater treatment systems, which often don't have the resources to apply well-established nutrient removal processes. WTRs, a water industry byproduct, have been studied for the ability to reduce nutrients from both point and non-point sources. The beneficial use of WTRs provides a possible solution for nutrient control practices.

5.1 Regulations

WTR has not been directly regulated at the federal level and was especially exempted from the biosolid disposal regulations (U.S. EPA, 1996). It is the states that are responsible for waste regulation. In Colorado, WTR management and beneficial use are prompted by regulations for solid waste and administered under the Water Quality Control Division of the Colorado Department of Public Health and Environment (CDPHE). In order to apply beneficial use practices, a Beneficial Use Plan must be

submitted, and authorization from CDPHE must be obtained. According to the regulation document 5 CCR 1003-7, a Beneficial Use Plan shall contain the information of the producers and contractors, a legal description of the application practice, and the characterization of the WTRs. WTRs must be identified for a series of parameters including pH, P, N, As, metals (e.g. Al, Fe and Cd), and total Alpha Activity (pCi/g). Possible presence of radionuclides in WTRs is of concern in Colorado. Radioactive WTR management is guided by Technologically-Enhanced Naturally Occurring Radioactive Materials (TENORM) regulations in Colorado and the federal government. As a result, for the development of a beneficial use application of WTR, these regulation conditions must be considered. Generally, the procedure that could be followed to develop a beneficial use application of WTR is shown in Figure 5-1.
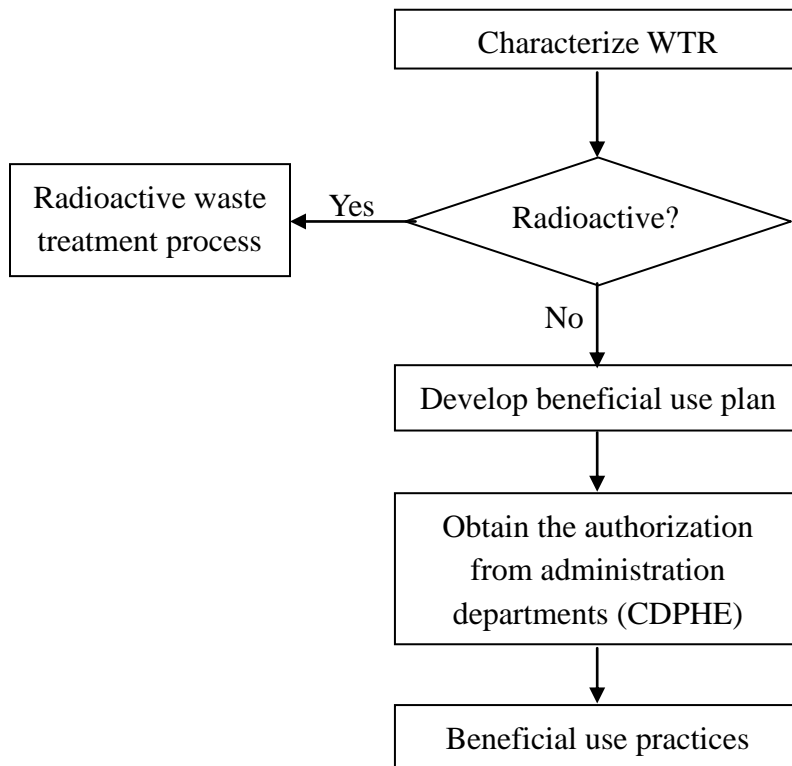
Figure 5-1 Procedure of beneficial use development for WTRs

5.2 Studies on the pathways of beneficial use

The beneficial use pathways of WTRs have been investigated in various studies. WTRs have been proven to be capable of mitigating nutrient contamination issues in both engineered and natural environments. The beneficial use of WTRs for nutrient control possesses the advantages of cost-effectiveness and easy operation. Figure 5-2 summarizes the potential pathways for this purpose.
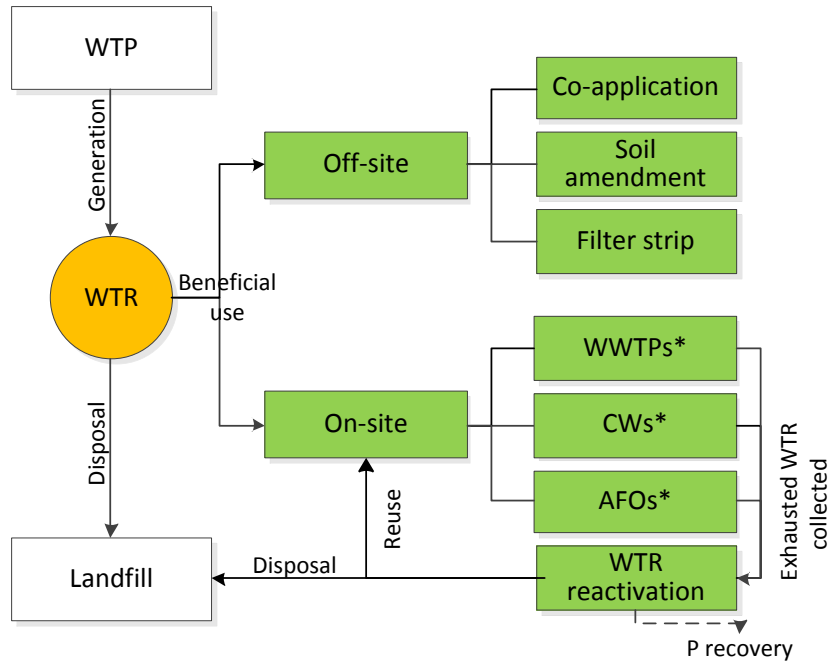
Figure 5-2 Proposed pathways of beneficial use of WTRs for nutrient control (*WWTPs – wastewater treatment plants, *CWs – constructed wetlands, *AFOs – Animal feed operation)

After being identified, the non-hazardous WTRs can be beneficially used for the purpose of nutrient control. In on-site applications, WTR is a cost-effective option to enhance the effluent quality in existing wastewater treatment systems. In off-site situations, WTR amendment of soils or bio-solids can help control the non-point source nutrients. More details of the application methods are discussed below.

5.2.1 Applications On-site wastewater treatment systems

Being capable of providing effective long-term treatment with low maintenance, the application of WTR filters for onsite nutrient removal in wastewater is considered economically and technically compatible with current onsite designs (Chang et al., 2010). Thus, WTR applications can be easily supplemented into existing wastewater treatment

systems as an improvement for nutrient control.

5.2.1.1 Effluent polishing

As discussed in Chapter 1, traditional nutrient removal methods are often unaffordable in small-scale wastewater treatment systems because of cost and technology requirements. WTR applications provide an easy but cost-effective solution to reduce nutrient levels in effluent.

Mortula and Gagnon (2007) investigated the use of Al-WTR for P adsorption from secondary municipal wastewater effluent and aquaculture processing water with bench-scale experiments (batch and fixed-bed column tests). The results indicated 91 to 98% orthophosphate removals, low impact on effluent pH, low Al leaching level (<0.5 mg L-1), and the ability to sorb organic materials from process waters and reduce biochemical oxygen demand.

Baker et al. (1998) proposed the concept of "Permeable Reactive Mixtures" for phosphorus removal from onsite wastewater disposal systems. Although the reactive mixtures investigated did not include WTR, the placements for the reactive filter media proposed by the author are inspirational for on-site WTR applications. For the purpose of reducing the impact of anthropogenic P on environments, the reactive media could be used (1) as an additional layer of septic system (Figure 5-3A), (2) for the effluent polishing after onsite wastewater treatment systems (Figure 5-3B) and (3) as the in-situ

treatment barrier for phosphate plumes (Figure 5-3C). However, other than laboratory

experiments, no data from real applications were reported.
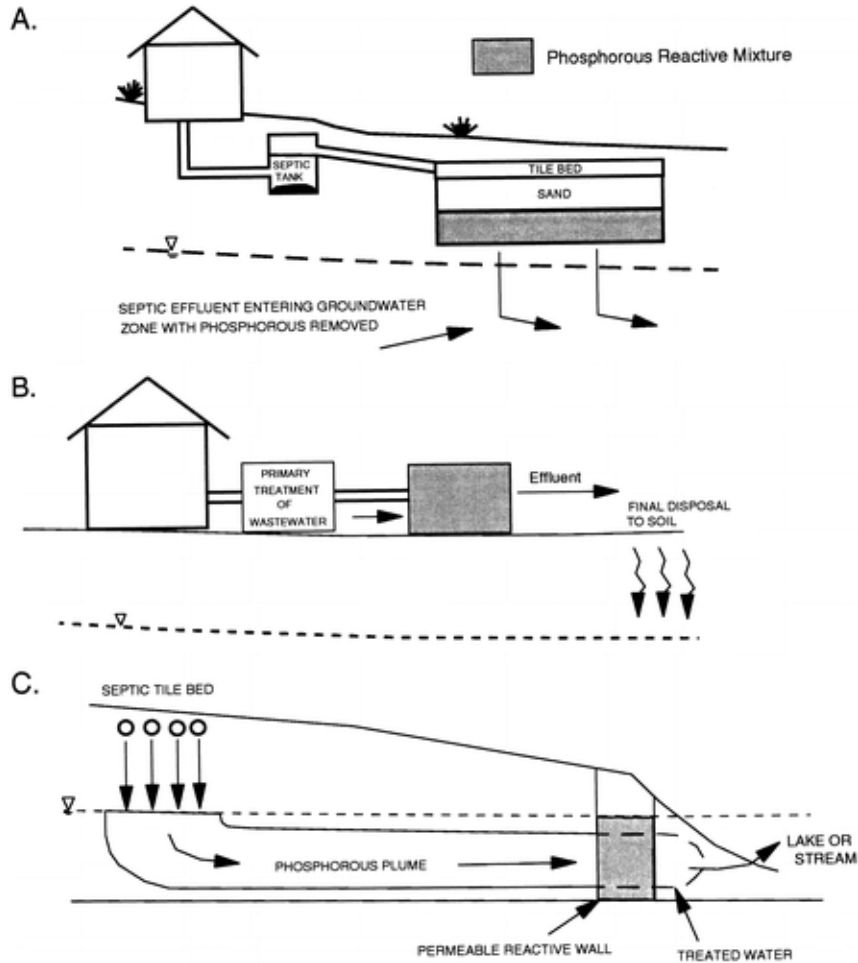
Figure 5-3 Placements for permeable reactive mixtures for P removal applied to onsite wastewater treatment (Baker et al., 1998)

5.2.1.2 Reduction for the concentrated nutrients in waste lagoons

Another possible application of WTRs is for the nutrient control in the waste lagoons

of animal feed operations (AFOs). Waste lagoons are a widely used method to store and

stabilize AFO wastewater. However, the concentrated N and P in waste lagoons have

become a concern for the potential to contaminant groundwater. WTR filters could be a solution to this problem, as illustrated in Figure 5-4. The wastewater in lagoons is continuously pumped into a circulation line and passed through a fixed-bed filter packed with WTRs. In this way N and P in the waste lagoons can be stripped out and maintained at relatively low levels.
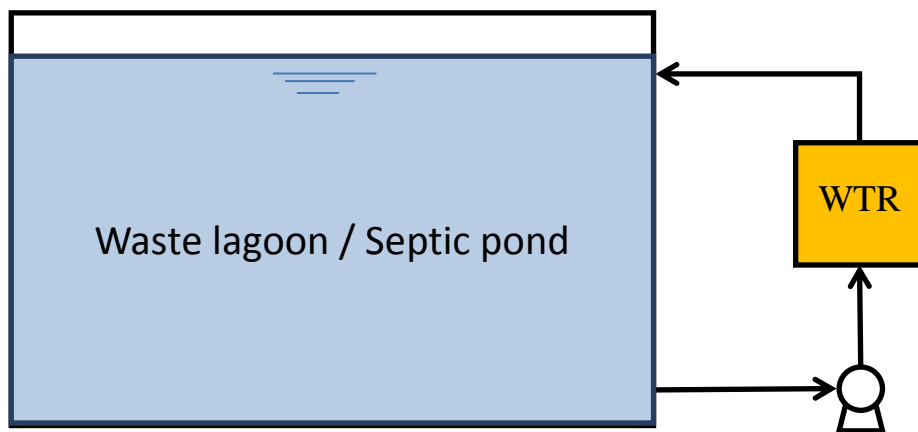
Figure 5-4 Circulation flow through WTR filters to reduce nutrient in waste lagoons

5.2.1.3 Substrates of constructed wetland

A possibility also exists for WTR usage as the substrate in constructed wetlands (CWs). CW integrated with WTR can achieve multi-functional removal with good efficiencies to the pollutants including BOD_5, COD, suspended solids, P and N (Park, 2009; Zhao et al. 2010).

In the research of Zhao et al. (2010), a field-scale CW with 65 cm of Al-WTR cakes

as the main substrate layer was used to treat wastewater from an animal research farm. The system was operated as a sub-surface flow system using a tidal flow operation. For a one-year period, the mean monthly removal efficiencies for various contaminants were BOD_5 57–84%, COD 36–84%, TN 11–78%, NH_4-N 49–93%, TP 75–94%, inorganic P 73–97% and suspended solids 46–83%.

Other than the substrate uses of CWs, WTR was also designed as a filter media to improve the treatment performance of CWs. Park (2009) utilized WTR in pre- and post-filter units, integrated in CW systems with oyster shells as the substrate. During the experimental period, the polishing effect of effluent water quality could be observed with the integrated WTR filters. The removal efficiencies of the influent BOD_5, N, P and suspended solids for pre-filter setup and post-filter setup were 89.3%, 68.8%, 99.4% and 89.9%, and 91.4%, 93.2%, 99.7% and 73% removals, respectively. The post-filter setup demonstrated better performance for N removal.

5.2.2 Off-site applications for non-point source (NPS) control

In the areas with soil types that are characterized with poor P-retention capacity, anthropogenic P from nonpoint sources can be easily transported via leaching or surface runoff and eventually contaminate natural waters. Land application of WTRs can be a cost-effective solution for immobilization of P in soil by increasing P sorption capacity in the WTR-amended soils (Elliott and Dempsey, 1991; Dayton and Basta, 2005; Novak and

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Watts, 2005).

Agyin-Birikorang et al. (2009) conducted an experiment in natural field conditions to investigate the accumulation of P from 4 sources of different surface soil and shallow ground water with and without WTR amendment. With the application of Al-WTR, the soluble P concentration was reduced both in soil and the shallow ground water. Meanwhile, the presence of Al-WTR amendment did not affect the dissolved Al level in the ground water during the study period. Actually, Mortula's research (2007) revealed that phosphorus treatment of alum residuals reduced its aluminum leachability and therefore, reduced the potential risk of aluminum contamination from reuse or disposal of treated alum residuals. There have also been concerns about the stability of P-sorbed WTRs and the potential release of P back to the environment. Miller et al. (2010) found the P desorption of the investigated Al-WTR was less than 2% of the total P sorbed when cumulative P loadings were less than 40 g/kg, and less than 9% when cumulative P loadings exceeded 70 g/kg. The author concluded that Al-WTR is an ideal medium of the permeable reactive barrier (PRB) for the purpose of reducing P losses to groundwater and estimated a lifespan of many decades for Al-WTR PRBs under these conditions.

A study on long-term phosphorus immobilization was conducted at several manure-impacted fields in Michigan (Agyin-Birikorang et al., 2006). After the WTR amendment was applied to the surface soil in 1998, the P removal effect remained stable

for 7.5 years and the water soluble P was reduced by over 60% as compared to the control plots. The WTR-immobilized P would remain stable as long as the WTR particles are not destroyed by extreme conditions (Agyin-Birikorang et al., 2006).

5.2.3 P recovery and WTR Regeneration

P recovery has economic and environmental benefits since P is a resource whose supply is becoming limited. For P recovery purposes, Zhao et al. (2009) studied the P desorption of a P-saturated WTR, which was used as the main substrate of constructed wetlands. Groups of batch experiments were designed and conducted to explore the efficiencies of P extraction using different acids (HCl, HNO_3 and H_2SO_4) and bases (NaOH and KOH). The results showed that either acid or base is efficient for P extraction and the efficiency relied mainly on the concentrations of H^+/OH^-, not the type of acid or base. H_2SO_4 was chosen as an efficient and cost-effective reagent for P extraction. At such optimal condition, the maximum P extraction efficiency of 98.2% was achieved.

However, in addition to the total P desorption, most of the main components of the saturated sludge, such as metals (Al, Ca, Mg and Fe), TOC (total organic carbon) and nitrogen can also be extracted. The results indicated approximately 100% of the metal-Al which seems to be the backbone of the WTR particles were extracted from the WTR, suggesting that near complete dissolution but not extraction was taking place upon the use of the strong sulfuric acid. Plus, the optimal condition for H_2SO_4 extraction

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determined by response surface methodology in this study may prove inadequate to even partially extract a significant portion of total P from the substrate-WTR in real and field situation since the pH-buffering capacity of the wastewater in the wetland may be much greater (Zhao et al., 2009).

Nevertheless, P reclamation from WTR and regeneration of the WTR's adsorption capacity (at least partially) are possible and are an important area of research to make a filter with this material viable. A schematic of a proposed reclamation/regeneration system is shown in Figure 5-5. Besides the pathway of water usage and treatment, a chain of WTRs reuse and regeneration could also be established. It not only serves as a new waste disposal option, but also achieves P removal and recovery.
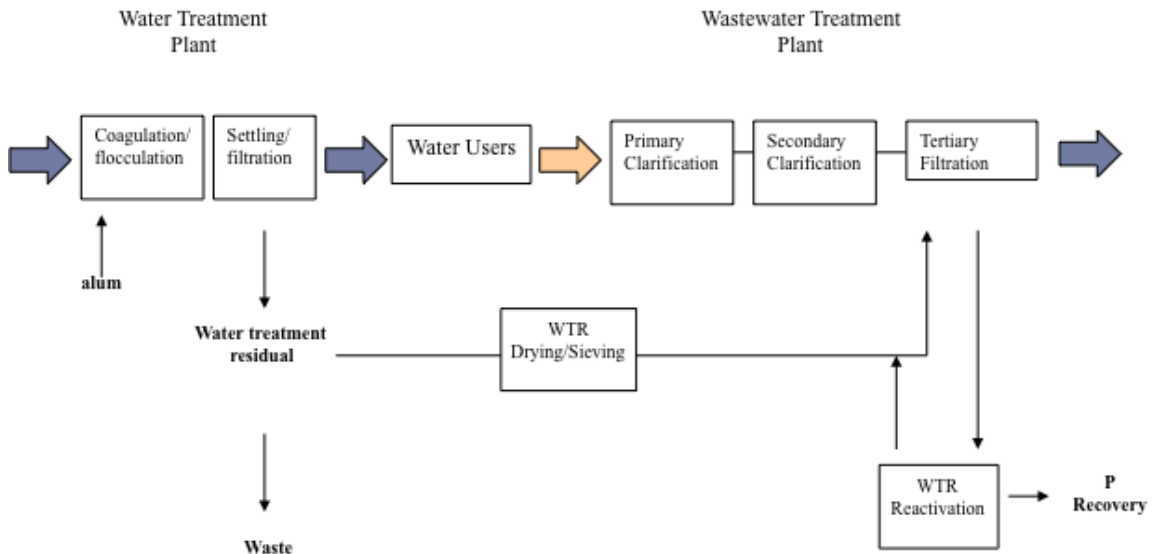
Figure 5-5 Proposed P Reclaim and WTR Regeneration System

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Chapter 6   CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The main objective of this research project was to evaluate the phosphorus (P) and nitrogen (N) removal capabilities of an aluminum based water treatment residual (Al-WTR) as filter media in fixed-bed filters. The characterization of the Al-WTR was investigated, and batch and column experiments were conducted to study the P and N removal performances in wastewaters and synthetic solutions. The conclusions are:

(1) The Al-WTR had high concentrations of total Al and TOC, thus being able to facilitate P sorption and biological denitrification simultaneously. The hydraulic conductivity of Al-WTR was acceptable for filter media usage.

(2) Batch experiments indicate Al-WTR was a better sorbent for orthophosphate phosphorus (RP) than total phosphorus (TP). The maximum sorption densities obtained at pH of 4, 7, and 9 respectively were 3.833, 3.258 and 2.038 mg/g.

(3) In column tests, a long-duration experiment proved that even very small ratios of Al-WTR (5%) amendment in sand could significantly improve the P reduction efficiency.

In column tests, the filter media demonstrated better sorption performance for RP than TP, which is consistent with the batch results. However, in these column tests, the sorption density values (average 15.74 mg/g) were much higher than the maximum sorption capacity results obtained in batch tests. This could be due to the different contact conditions of equilibrium reaction and continuous-flow reaction for sorbent and sorbate. The result suggested that the isotherms determined using batch methods cannot predict the sorption capacity for continuous-flow conditions well.

(4) Simultaneous P and N removal was achieved in column tests with high efficiencies for P (95.99% for RP and 90.04 % for TP) and N (99.62% for nitrate). WTR demonstrated much better performance compared to sand as filter media.

In sum, this study showed that Al-WTR is a promising filter medium (or amendment) for P and N reduction in wastewater.

6.2 Recommendations

The recommendations for future work include:

(1) Regarding the maximum sorption density (Q_{max}), there are inconsistencies between batch results and column results. The former ones are significantly lower than the latter ones. Higher initial concentrations may be adopted for the batch equilibrium tests to see the possible difference.

(2) Investigate the possible improvements for P and N removal in the column

experiments by adjusting the parameters, such as hydraulic residence time, media

composition and media depth.

(3) Investigate the growth of biofilm in the filter media and identify the possible

difference between WTR-packed and sand-packed columns.

(4) Develop field-scale tests based on the bench-scale ones of this study.

(5) Optimize the method for reclamation of P and the regeneration of WTR. Investigate

the proper conditions for dissolving P including pH, contact duration, and dosages.

REFERENCE

Agyin-Birikorang, S., O.O. Oladeji, G.A. O'Connor, T.A. Obreza and J.C. Capece. 2009. Efficacy of Drinking-Water Treatment Residual in Controlling Off-Site Phosphorus Losses: A Field Study in Florida. Journal of Environmental Quality. 38: 3: 1076-1085.

Agyin-Birikorang, Sampson., George A. O'Connor, Lee W. Jacobs, Konstantinos C. Makris, and Scott R. Brinton. 2007. Long-Term Phosphorus Immobilization by a Drinking Water Treatment Residual. J. Environ. Qual. 36: 316–323.

American Public Health Asssociation (APHA). 1992. Standard methods for the examination of water and wastewater. 18th ed. Washington, DC.

Baalsrud, K., and K.S. Baalsrud. 1954. Studies on Thiobacillus denitrificans. Archives of Microbiology. 20: 34-62.

Babatunde, A.O. and Y.Q. Zhao. 2007. Constructive approaches towards water treatment works sludge management: a review of beneficial reuses, Crit. Rev. Environ. Sci. Technol. 37: 129–164.

Babatunde, A.O., Y.Q. Zhao, A.M. Burke, M.A. Morris and J.P. Hanrahan. 2009. Characterization of aluminum-based water treatment residual for potential phosphorus removal in engineered wetlands. Environmental Pollution. 157: 10: 2830-2836.

Babatunde, A.O., Y.Q. Zhao, A.M. Burke, M.A. Morris, J.P. Hanrahan. 2009. Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. Environmental Pollution. 157: 10: 2830-2836.

Baker, Michael J., David W. Blowes, Carol J. Ptacek. 1998. Laboratory Development of Permeable Reactive Mixtures for the Removal of Phosphorus from Onsite Wastewater Disposal Systems Environ. Sci. Technol. 32: 15: 2308–2316.

Basibuyuk, M., Kalat, D.G. 2004. The use of waterworks sludge for the treatment of vegetable oil refinery industry wastewater. J. Environ. Technol. 25: 3: 373-380.

Benjamin, Mark M. 2002. Water Chemistry. Boston: McGraw-Hill.

Blomqvist, Sven., Anneli Gunnars and Ragnar Elmgren. 2004. Why the limiting nutrient differs between temperate coastal seas and freshwater lakes: A matter of salt. Limnology and Oceanography. 49: 6: 2236-2241.

Boley, A., W.R. Müller and G. Haider. 2002. Biodegradable polymers as solid substrate and biofilm carrier for denitrification in recirculated aquaculture systems. Aquacul. Eng. 22: 75–85.

Carlson, C. A., and J. L. Ingraham. 1983. Comparison of denitrification by Pseudomonas stutzeri, Pseudomonas aeruginosa, and Paracoccus denitrificans. Appl. Environ. Microbiol. 45: 1247-1253.

Carpenter, S.R. and Bennett E.M. 2011. Reconsideration of the planetary boundary for phosphorus. Environmental Research Letters 6: 1: 1-12.

Centers for Disease Control and Prevention (CDC). 2004. About Harmful Algal Blooms (HABs). http://www.cdc.gov/hab/about.htm.

Chang, Ni-Bin, Fahim Hossain, Marty Wanielista. 2010. Filter Media for Nutrient Removal in Natural Systems and Built Environments: I – Previous Trends and Perspectives. Environmental Engineering Science. 27: 9: 689-706.

Correll, David L. 1998. The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review. J. Environ. Qual. 27: 261-266.

Dayton, E.A., Basta, N.T. 2001. Characterization of drinking water treatment residuals for use as a soil substitute. Water Environ. Res. 73: 52-57.

Della Rocca, C., V. Belgiorno, S. Meric. 2005. Cotton-supported heterotrophic denitrification of nitrate-rich drinking water with a sand filtration post-treatment. Water SA. 31: 2: 229–236.

Dewolfe, J. 2006. Water Residuals to Reduce Soil Phosphorus, AWWARF, Denver, Colorado.

Elliott, H.A., B.A. Dempsey. 1991. Agronomic Effects of Land Application of Water Treatment Sludges. J. Am. Water Wlorks Assoc. 84: 3: 126.

Firestone, M. K. 1982. Biological denitrification. In: Nitrogen in agricultural soils. Monograph No. 22. American Society of Agronomy, Madison, WI.

Graham, Jennifer L. 2007. Harmful Algal Blooms. U.S. Geological Survey (USGS) Fact Sheet 2006–3147.

Guan, Xiaohong. 2005. Adsorption of phosphates and organic acids on Aluminum

hydroxide in aquatic environment – mechanism and interactions. Ph.D dissertation. Hong Kong University of Science and Technology.

Hunter, J. V., Heukelekian H. 1965. The compostion of domestic sewage fractions. J. Water Pol. Control Fed. 37: 1142-1163.

Jenkins, David. John f. Ferguson, Arnold B. Menar. 1971. Chemical processes for phosphate removal. Water Research Pergamon Press. 5: 369-389.

Klute, A. 1986. Hydraulic conductivity: Laboratory Methods. Methods of Soil Analysis. 2nd Ed., A. Klute (Ed), Soil Sci. Soc. Am., Madison, Wis.

Makris, K.C., D.Sarkar, R.Datta. 2006. Evaluating a drinking-water waste by-product as a novel sorbent for arsenic. Chemosphere. 64: 730–741.

Makris, K.C., G.A. O'Connor. 2007. Beneficial utilization of drinking-water treatment residuals as contaminant-mitigating agents, Dev. Environ. Sci. 5: 609–655.

Makris, K.C., W.G. Harris, G.A. O'Connor, T.A. Obreza, H.A. Elliott. 2005. Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals, Environ. Sci. Technol. 39: 4280.

Miller, Matthew L., Jehangir H. Bhadha, George A. O'Connor, James W. Jawitz, Jennifer Mitchell. 2011. Aluminum water treatment residuals as permeable reactive barrier sorbents to reduce phosphorus losses. Chemosphere. 83: 978–983.

Mortula, M.M., G.A. Gagnon. 2007. Alum residuals as a low technology for phosphorus removal from aquaculture processing water. Aquacultural Engineering. 36: 3: 233-238.

Nair, P.S., T.J. Logan, A.N. Sharpley, L.E. Sommers, M.A. Tabatabai, T.L.Yuan. 1984. Interlaboratory Comparison of a Standardized Phosphorus Adsorption Procedure. J. Environ. Qual. 13: 4: 591-595.

Novak, J. M., D.W. Watts. 2005. An Alum-Based Water Treatment Residual Can Reduce Extractable Phosphorus Concentrations in Three Phosphorus-Enriched Coastal Plain Soils. J. Environ. Qual. 34: 1820–1827.

O'Connor, G.A., H.A. Elliott, and P. Lu. 2002. Characterizing water treatment residuals phosphorus retention. Proc. Soil Crop Sci. Soc. Fla. 61: 67–73.

Page, A. L. 1982-1986. Methods of Soil Analysis. 2nd ed. Madison. American Society of Agronomy.

Parfitt, R.L., Atkinson, R.J. and Smart, R.S.C. 1975. The mechanism of phosphate fixation by iron oxides. Soil Sci. Soc. Am. Proc. 39: 837-841.

Park, W.H. 2009. Integrated constructed wetland systems employing alum sludge and

oyster shells as filter media for P removal, Ecol Eng. 35: 1275–1282.

Pidwirny, M., S. Jones. 2006. The Nitrogen Cycle. Fundamentals of Physical Geography, 2nd Edition. http://www.physicalgeography.net/fundamentals/contents.html.

Pierzynski, Gary M., J. Thomas Sims, George F. Vance. 2005. Soils and environmental quality, 3th ed, Taylor & Francis Group, LLC.

Prakash, P., Sengupta, A.K. 2003. Selective coagulant recovery from water treatment plant residuals using Donnan membrane process. Environ. Sci. Technol. 37: 4468-4474.

Rajan, S.S.S., K.W. Perrott, W.M.H. Saunders. 1974. Identification of phosphate-reactive sites of hydrous alumina from proton consumption during phosphate adsorption at constant pH values. J. Soil Sci. 25: 438-447.

Razali, M., Y.Q. Zhao, M. Bruen. 2007. Effectiveness of a drinking-water treatment sludge in removing different phosphorus species from aqueous solution. Separation and Purification Technology. 55: 300–306.

Reddi, Lakshmi N. 2005. Animal Waste Containment in Lagoons. Reston, VA, American Society of Civil Engineers.

Redfield, A.C. 1934. On the proportions of organic derivations in sea water and their relation to the composition of plankton. In James Johnstone Memorial Volume. (ed. R.J. Daniel). University Press of Liverpool. 177-192.

Sedlak, R. 1991. Phosphorus and nitrogen removal from municipal wastewater: principles and practice. 2nd ed. Chelsea, Mich.: Lewis Publishers.

Thurston, Robert V., Rosemarie C. Russo, G. A. Vinogradov. 1981. Ammonia toxicity to fishes. Effect of pH on the toxicity of the unionized ammonia species. Environ. Sci. Technol. 15: 7: 837–840.

U.S. Army Corps of Engineers (USACE). 2001. Biological Nutrient Removal. Public Works Technical Bulletin 420-49-39.

U.S. EPA. 2005. A Regulators' Guide to the Management of Radioactive Residuals from Drinking Water Technologies. EPA 816-R-05-004.

U.S. EPA. American Association of Civil Engineers (ASCE), American Water Works Association (AWWA). 1996. Technology Transfer Handbook: Management of Water Treatment Plant Residuals. EPA 625/R-95/008.

Vohla, Christina, Margit Kõiv, H. John Bavor, Florent Chazarenc, Ülo Mander. 2009. Filter materials for phosphorus removal from wastewater in treatment wetlands—A review. Ecological Engineering, in Press.

Water Environment Federation (WEF). 1998. Biological and Chemical Systems for Nutrient Removal, Water Environment Federation, Alexandria, VA.

Westholm, L.J. 2006. Substrates for phosphorus removal—Potential benefits for on-site wastewater treatment? Water Research, 40: 23 – 36.

Yang, Ralph T. 2003. Adsorbents Fundamentals and Applications. New Jersey, John Wiley & sons, Inc.

Yang, Y., A.O. Babatunde, Y.S. Hu, J.L.G. Kumar, X.H. Zhao. In Press. Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatment. Process Biochemistry. In Press.

Yang, Y., Y.Q. Zhao, A.O. Babatunde, L. Wang, Y.X. Ren, Y. Han. 2006. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. Separation and Purification Technology. 51: 2: 193-200.

Yarkin, M., K. Carlson. 2008. Enhancing natural treatment systems by utilizing water treatment residuals. PhD's Dissertation. Colorado State University, Fort Collins, CO.

Yeoman, S., Stephenson, T., Lester, J. N., Perry, R., 1988. The Removal of Phosphorus during Wastewater Treatment: A Review, Environmental Pollution, 49: 183-233.

Zhao, X.H., Y.Q. Zhao. 2009. Investigation of phosphorus desorption from P-saturated alum sludge used as a substrate in constructed wetland. Separation and Purification Technology. 66: 71–75.

Zhao,Y.Q., A.O. Babatunde, Y.S. Hu, J.L.G. Kumar, X.H. Zhao. 2011. Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatment. Biochemistry. 46: 278–283.

APPENDIX:

COLUMN EXPERIMENT DATA

Table 1 Data of Column C0

Day	Influent RP (mg/L)	Effluent RP (mg/L)	Removal rate (%)	Sorption density (mg/g)	TOC (mg/L)	TN (mg/L)	Al (mg/L)	Pore Volumes
1	4.47	0.46	89.8	-	16.33	22.39	-	3.5
2	4.47	3.15	29.6	-	12.52	21.97	-	17.6
5	4.54	4.18	7.9	-	6.15	2.234	-	31.7
8	4.44	4.18	5.9	-	7.43	0.872	-	45.7
11	4.41	4.27	3.0	-	4.29	0.892	-	59.8
14	4.24	4.11	3.1	-	5.9	0.837	-	73.9
17	4.01	3.92	2.4	-	6.92	0.855	-	88.0
20	4.14	4.01	3.1	-	4.375	0.361	-	102.0
23	4.41	4.37	0.7	-	4.496	0.281	-	116.1
26	4.11	4.05	1.6	-	4.196	0.421	-	130.2
29	4.18	4.11	1.6	-	4.537	0.314	-	144.3
32	4.14	4.08	1.6	-	-	-	-	158.4
35	4.27	4.24	0.8	-	-	-	-	172.4
38	4.01	4.08	-1.6	-	-	-	-	186.5
41	4.27	4.24	0.8	-	-	-	-	200.6
44	4.01	4.01	0.0	-	-	-	-	214.7
47	4.01	4.05	-0.8	-	-	-	-	228.7
50	3.92	3.92	0.0	-	-	-	-	242.8
53	3.75	3.69	1.7	-	-	-	-	256.9
56	3.82	3.82	0.0	-	-	-	-	271.0
59	3.85	3.85	0.0	-	-	-	-	285.0
62	4.50	4.44	1.4	-	-	-	-	299.1
65	4.50	4.47	0.7	-	-	-	-	313.2
68	4.47	4.47	0.0	-	-	-	-	327.3
71	4.47	4.44	0.7	-	-	-	-	341.3
74	4.34	4.37	-0.8	-	-	-	-	355.4
Average	4.22	3.96	5.9	-	7.01	4.68	-	-
S. D.	0.24	0.77	18.1	-	3.93	8.67	-	-

Table 2 Data of Column C5

Day	Influent RP (mg/L)	Effluent RP (mg/L)	Removal rate (%)	Sorption density (mg/g)	TOC (mg/L)	TN (mg/L)	Al (mg/L)	Pore Volumes
1	4.47	0.06	98.6	0.12	62.54	26.88	-	3.5
2	4.47	0.04	99.1	2.72	24.18	22.98	-	17.6
5	4.54	0.07	98.6	6.09	13.09	1.564	-	31.7
8	4.44	0.08	98.2	9.45	11.527	0.537	-	45.7
11	4.41	0.20	95.5	12.79	7.494	0.475	-	59.8
14	4.24	0.16	96.2	16.02	5.94	0.535	-	73.9
17	4.01	0.13	96.7	19.11	5.198	0.511	-	88.0
20	4.14	0.11	97.2	22.31	4.502	0.432	-	102.0
23	4.41	0.21	95.2	25.71	4.088	0.359	-	116.1
26	4.11	0.45	89.0	28.65	4.421	0.22	-	130.2
29	4.18	0.62	85.2	31.50	4.29	0.327	-	144.3
32	4.14	0.61	85.4	34.34	-	-	-	158.4
35	4.27	1.35	68.5	36.71	-	-	-	172.4
38	4.01	1.75	56.5	38.61	-	-	-	186.5
41	4.27	2.10	50.8	40.36	-	-	-	200.6
44	4.01	2.43	39.4	41.65	-	-	-	214.7
47	4.01	2.55	36.6	42.88	-	-	-	228.7
50	3.92	2.25	42.5	44.24	-	-	-	242.8
53	3.75	2.07	44.8	45.56	-	-	-	256.9
56	3.82	1.91	50.0	47.12	-	-	-	271.0
59	3.85	1.95	49.3	48.67	-	-	-	285.0
62	4.50	3.07	31.9	49.80	-	-	-	299.1
65	4.50	2.58	42.8	51.35	-	-	-	313.2
68	4.47	2.38	46.7	53.05	-	-	-	327.3
71	4.47	2.61	41.6	54.55	-	-	-	341.3
74	4.34	2.38	45.1	56.17	-	-	-	355.4
Average	4.22	1.31	68.5	33.06	13.39	4.98	-	-
S. D.	0.24	1.08	25.7	17.18	17.38	9.91	-	-

Table 3 Data of Column C10

Day	Influent RP (mg/L)	Effluent RP (mg/L)	Removal rate (%)	Sorption density (mg/g)	TOC (mg/L)	TN (mg/L)	Al (mg/L)	Pore Volumes
1	4.47	0.04	99.2	0.08	101.47	29.08	0.004	3.5
2	4.47	0.04	99.2	1.41	31.57	22.28	-	17.6
5	4.54	0.05	98.9	3.12	20.27	1.114	-	31.7
8	4.44	0.02	99.6	4.83	15.78	0.574	-	45.7
11	4.41	0.03	99.3	6.57	10.37	0.549	-	59.8
14	4.24	0.03	99.2	8.24	8.11	0.587	-	73.9
17	4.01	0.03	99.3	9.84	6.88	0.52	-	88.0
20	4.14	0.04	99.1	11.47	4.767	0.384	-	102.0
23	4.41	0.02	99.5	13.25	3.969	0.317	-	116.1
26	4.11	0.03	99.3	14.90	3.346	0.251	-	130.2
29	4.18	0.04	99.1	16.57	3.614	0.242	-	144.3
32	4.14	0.10	97.6	18.20	-	-	-	158.4
35	4.27	0.10	97.6	19.89	-	-	-	172.4
38	4.01	0.09	97.7	21.52	-	-	-	186.5
41	4.27	0.18	95.9	23.19	-	-	-	200.6
44	4.01	0.35	91.3	24.69	-	-	-	214.7
47	4.01	0.38	90.5	26.18	-	-	-	228.7
50	3.92	0.40	89.7	27.62	-	-	-	242.8
53	3.75	0.53	85.8	28.92	-	-	-	256.9
56	3.82	0.52	86.4	30.27	-	-	-	271.0
59	3.85	0.49	87.2	31.64	-	-	-	285.0
62	4.50	0.65	85.5	33.19	-	-	-	299.1
65	4.50	0.59	87.0	34.78	-	-	-	313.2
68	4.47	0.57	87.2	36.38	-	-	-	327.3
71	4.47	0.61	86.4	37.94	-	-	-	341.3
74	4.34	0.63	85.5	39.47	-	-	-	355.4
Average	4.22	0.25	94.0	20.16	19.10	5.08	0.00	-
S. D.	0.24	0.25	5.8	12.08	28.67	10.30	-	-

Table 4 Data of Column C15

Day	Influent RP (mg/L)	Effluent RP (mg/L)	Removal rate (%)	Sorption density (mg/g)	TOC (mg/L)	TN (mg/L)	Al (mg/L)	Pore Volumes
1	4.47	0.04	99.1	0.07	126.27	32.69	0.014	3.5
2	4.47	0.03	99.3	0.97	45.26	22.15	-	17.6
5	4.54	0.03	99.3	2.12	23.63	1.343	-	31.7
8	4.44	0.04	99.1	3.26	17.7	0.672	-	45.7
11	4.41	0.03	99.3	4.42	12.39	0.697	-	59.8
14	4.24	0.04	99.2	5.54	10.19	0.682	-	73.9
17	4.01	0.03	99.3	6.60	8.42	0.736	-	88.0
20	4.14	0.03	99.4	7.69	7.909	0.873	-	102.0
23	4.41	0.03	99.3	8.88	4.882	0.378	-	116.1
26	4.11	0.03	99.3	9.98	4.444	0.31	-	130.2
29	4.18	0.04	99.1	11.09	3.598	0.243	-	144.3
32	4.14	0.04	99.1	12.19	-	-	-	158.4
35	4.27	0.07	98.4	13.33	-	-	-	172.4
38	4.01	0.06	98.6	14.43	-	-	-	186.5
41	4.27	0.11	97.3	15.55	-	-	-	200.6
44	4.01	0.15	96.3	16.61	-	-	-	214.7
47	4.01	0.17	95.9	17.66	-	-	-	228.7
50	3.92	0.24	93.9	18.67	-	-	-	242.8
53	3.75	0.36	90.5	19.58	-	-	-	256.9
56	3.82	0.36	90.6	20.52	-	-	-	271.0
59	3.85	0.31	91.9	21.49	-	-	-	285.0
62	4.50	0.36	92.1	22.60	-	-	-	299.1
65	4.50	0.31	93.1	23.74	-	-	-	313.2
68	4.47	0.32	92.9	24.87	-	-	-	327.3
71	4.47	0.35	92.2	25.99	-	-	-	341.3
74	4.34	0.37	91.6	27.08	-	-	-	355.4
Average	4.22	0.15	96.4	13.65	24.06	5.52	0.01	-
S. D.	0.24	0.14	3.4	8.26	35.98	11.08	-	-

Table 5 Data of Column C20

Day	Influent RP (mg/L)	Effluent RP (mg/L)	Removal rate (%)	Sorption density (mg/g)	TOC (mg/L)	TN (mg/L)	Al (mg/L)	Pore Volumes
1	4.47	0.04	99.1	0.06	144.64	36.34	0.022	3.5
2	4.47	0.03	99.4	0.76	59.79	21.07	-	17.6
5	4.54	0.03	99.3	1.62	29.14	1.478	-	31.7
8	4.44	0.01	99.7	2.48	20.68	0.73	-	45.7
11	4.41	0.03	99.4	3.35	13.3	0.682	-	59.8
14	4.24	0.03	99.3	4.20	9.34	0.644	-	73.9
17	4.01	0.03	99.3	4.99	8.17	0.698	-	88.0
20	4.14	0.04	99.0	5.81	7.12	21.1	-	102.0
23	4.41	0.04	99.1	6.70	7.02	23.41	-	116.1
26	4.11	0.04	99.1	7.52	5.16	16.61	-	130.2
29	4.18	0.04	99.1	8.36	4.51	5.317	-	144.3
32	4.14	0.06	98.7	9.19	-	-	-	158.4
35	4.27	0.04	99.2	10.05	-	-	-	172.4
38	4.01	0.03	99.3	10.87	-	-	-	186.5
41	4.27	0.03	99.3	11.74	-	-	-	200.6
44	4.01	0.04	98.9	12.55	-	-	-	214.7
47	4.01	0.07	98.4	13.36	-	-	-	228.7
50	3.92	0.06	98.4	14.15	-	-	-	242.8
53	3.75	0.06	98.5	14.90	-	-	-	256.9
56	3.82	0.05	98.7	15.67	-	-	-	271.0
59	3.85	0.10	97.5	16.43	-	-	-	285.0
62	4.50	0.13	97.2	17.32	-	-	-	299.1
65	4.50	0.18	96.0	18.20	-	-	-	313.2
68	4.47	0.21	95.3	19.07	-	-	-	327.3
71	4.47	0.20	95.6	19.94	-	-	-	341.3
74	4.34	0.20	95.4	20.79	-	-	-	355.4
Average	4.22	0.07	98.4	10.39	28.08	11.64	0.02	-
S. D.	0.24	0.06	1.4	6.33	41.93	12.55	-	-

Table 6 Data of Column Sand-WW

Date	Flow rate (L/min)	Pore Volumes	Influent(mg/l)			Effluent (mg/l)			Removal (%)		
			NO_3^--N	RP	TP	NO_3^--N	RP	TP	NO_3^--N	RP	TP
9/2/2010	0.28	6.1	15.4	2.32	2.53	8.2	0.23	0.31	46.8	90.1	87.9
9/3/2010	0.32	13.6	15.4	2.35	2.58	14.6	1.17	1.44	5.2	50.0	44.3
9/5/2010	0.31	27.1	14.9	2.35	2.53	5.3	1.34	1.81	64.4	43.1	28.4
9/7/2010	0.32	43.3	15.1	2.32	2.64	4.7	2.02	2.14	68.9	12.7	19.1
9/9/2010	0.31	57.6	14.4	2.02	2.66	0.2	1.99	2.04	98.6	1.6	23.3
9/11/2010	0.32	72.4	15	2.09	2.69	0.3	2.02	2.06	98.0	3.1	23.6
9/13/2010	0.31	87.2	14.8	2.06	2.51	0.8	2.06	2.24	94.6	0.0	11.0
9/15/2010	0.30	102.0	14.6	2.06	2.69	1.1	2.02	2.06	92.5	1.6	23.6
9/17/2010	0.28	115.2	14.5	2.22	2.74	0.6	2.12	2.20	95.9	4.4	19.6
9/19/2010	0.28	128.5	15.1	2.12	2.74	1.2	2.06	2.17	92.1	3.1	20.8
9/21/2010	0.28	142.0	14.8	2.03	2.65	0.9	2.02	2.29	93.9	3.1	20.8
9/23/2010	0.28	155.2	15.3	2.14	2.54	0.6	2.03	2.22	96.1	3.1	20.8
9/25/2010	0.27	168.6	15.2	2.10	2.55	0.6	2.06	2.20	96.1	3.1	20.8
Average	0.29	–	14.91	2.18	2.64	0.76	1.87	2.02	94.9	2.3	23.8
S. D.	0.02	–	0.29	0.13	0.09	0.30	0.35	0.25	2.0	1.6	9.0

Table 7 Data of Column WTR-WW

Date	Flow rate (L/min)	Pore Volumes	Influent (mg/l)			Effluent (mg/l)			Removal (%)		
			NO_3^--N	RP	TP	NO_3^--N	RP	TP	NO_3^--N	RP	TP
9/2/2010	0.23	3.3	15.4	2.32	2.53	1.4	0.07	0.48	90.9	97.0	80.9
9/3/2010	0.33	8.4	15.4	2.35	2.58	8.7	0.07	0.36	43.5	97.1	86.2
9/5/2010	0.30	17.2	14.9	2.35	2.53	1.8	0.04	0.26	87.9	98.5	89.8
9/7/2010	0.31	27.9	15.1	2.32	2.64	0	0.09	0.15	100.0	96.2	94.3
9/9/2010	0.31	37.4	14.4	2.02	2.66	0.4	0.18	0.32	97.2	91.3	87.9
9/11/2010	0.31	47.2	15	2.09	2.69	0.2	0.08	0.24	98.7	96.4	91.2
9/13/2010	0.30	56.9	14.8	2.06	2.51	0	0.08	0.26	100.0	96.2	89.6
9/15/2010	0.29	66.7	14.6	2.06	2.69	0	0.08	0.24	100.0	96.3	91.0
9/17/2010	0.28	75.4	14.5	2.22	2.74	0	0.08	0.29	100.0	96.6	89.3
9/19/2010	0.28	84.1	15.1	2.12	2.74	0.2	0.07	0.23	98.7	96.8	91.4
9/21/2010	0.27	92.9	14.8	2.03	2.65	0.1	0.07	0.27	99.3	96.8	91.4
9/23/2010	0.27	101.5	15.3	2.14	2.54	0.1	0.09	0.28	99.3	96.8	91.4
9/25/2010	0.27	110.2	15.2	2.10	2.55	0.1	0.08	0.27	99.3	96.8	91.4
Average	0.28	–	14.91	2.18	2.64	0.09	0.08	0.26	99.4	96.2	90.1
S. D.	0.02	–	0.29	0.13	0.09	0.08	0.04	0.06	0.6	2.0	2.3

Table 8 Data of Column Sand-SS

Date	Flow rate (L/min)	Pore Volumes	Influent (mg/l)			Effluent (mg/l)			Removal (%)		
			NO_3^--N	RP	TP	NO_3^--N	RP	TP	NO_3^--N	RP	TP
9/2/2010	0.28	6.1	14.7	2.35	–	13.7	0.46	–	6.8	80.6	–
9/3/2010	0.34	14.2	14.7	2.28	–	14.7	1.60	–	0.0	30.0	–
9/5/2010	0.33	28.3	14.8	2.32	–	14.6	1.93	–	1.4	16.9	–
9/7/2010	0.33	45.2	15	2.35	–	12.1	2.06	–	19.3	12.5	–
9/9/2010	0.33	60.3	14.7	2.28	–	13	1.96	–	11.6	14.3	–
9/11/2010	0.33	75.7	15.1	2.28	–	13.2	2.09	–	12.6	8.6	–
9/13/2010	0.32	91.2	15.3	2.32	–	15.3	2.19	–	0.0	5.6	–
9/15/2010	0.31	106.6	15.4	2.32	–	14.9	2.25	–	3.2	2.8	–
9/17/2010	0.30	120.7	15.5	2.35	–	15.5	2.19	–	0.0	6.9	–
9/19/2010	0.30	134.8	15.5	2.28	–	15.3	2.12	–	1.3	7.1	–
9/21/2010	0.29	148.9	15.1	2.28	–	14.2	2.09	–	6.0	7.1	–
9/23/2010	0.29	162.9	14.9	2.30	–	14.5	2.22	–	2.7	7.1	–
9/25/2010	0.29	176.9	15.3	2.28	–	15.1	2.15	–	1.3	7.1	–
Average	0.30	–	15.26	2.31	–	14.75	2.04	–	3.4	7.6	–
S. D.	0.02	–	0.21	0.03	–	0.76	0.20	–	2.1	3.8	–

Table 9 Data of Column WTR-SS

Date	Flow rate (L/min)	Pore Volumes	Influent (mg/l)			Effluent (mg/l)			Removal (%)		
			NO_3^--N	RP	TP	NO_3^--N	RP	TP	NO_3^--N	RP	TP
9/2/2010	0.23	3.3	14.7	2.35	–	2.9	0.07	–	80.3	97.2	–
9/3/2010	0.32	8.3	14.7	2.28	–	8.8	0.01	–	40.1	99.7	–
9/5/2010	0.30	17.1	14.8	2.32	–	3.2	0.01	–	78.4	99.6	–
9/7/2010	0.31	27.8	15	2.35	–	1.9	0.01	–	87.3	99.6	–
9/9/2010	0.31	37.2	14.7	2.28	–	3.9	0.04	–	73.5	98.3	–
9/11/2010	0.31	46.9	15.1	2.28	–	5.4	0.07	–	64.2	97.0	–
9/13/2010	0.30	56.6	15.3	2.32	–	5	0.02	–	67.3	99.3	–
9/15/2010	0.29	66.3	15.4	2.32	–	5.4	0.02	–	64.9	99.3	–
9/17/2010	0.28	75.1	15.5	2.35	–	5.4	0.03	–	65.2	98.8	–
9/19/2010	0.28	83.9	15.5	2.28	–	5.9	0.04	–	61.9	98.3	–
9/21/2010	0.28	92.9	15.1	2.28	–	5.3	0.05	–	64.9	98.3	–
9/23/2010	0.28	101.6	14.9	2.30	–	5.3	0.02	–	64.4	98.3	–
9/25/2010	0.27	110.4	15.3	2.28	–	5.3	0.02	–	65.4	98.3	–
Average	0.29	–	15.26	2.31	–	5.38	0.03	–	64.8	98.9	–
S. D.	0.01	–	0.21	0.03	–	0.25	0.02	–	1.5	0.9	–